Thin Films Technology

Lecture 4:
Physical Vapor Deposition PVD

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Contents

- Film growth mechanisms
- Different PVD methods
- Hard carbon films
- Commercial PVD coatings
- Scale up

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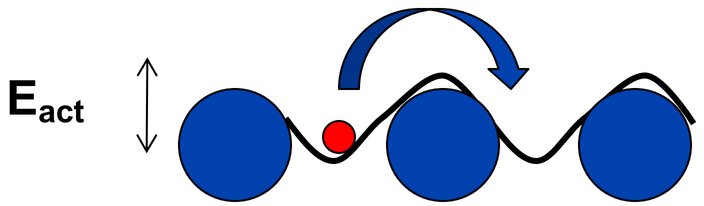
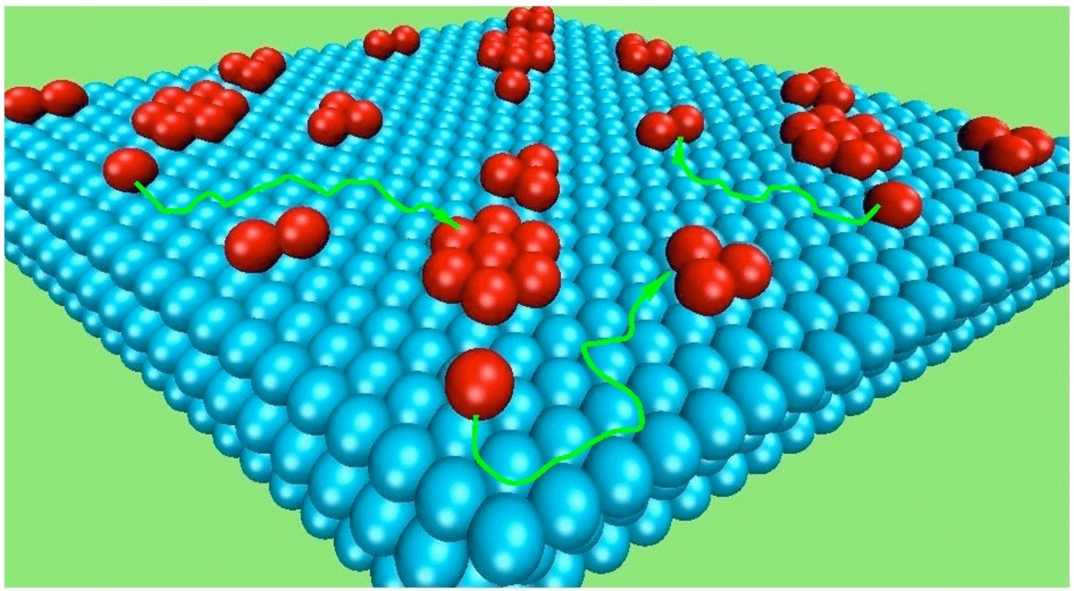
Surface diffusion

- Diffusion is thermally activated random movement of adsorbed atoms
- $D = D_0 e^{-E_{act}/kT}$
- E_{act} large -> slow diffusion
- T high – fast diffusion





http://iramis.cea.fr/spcsi/Phocea/Vie_des_labos/Ast/astimg.php?voir=60&type=groupe

Surface diffusion of Cu on Cu(111)

Coalescence - ripening

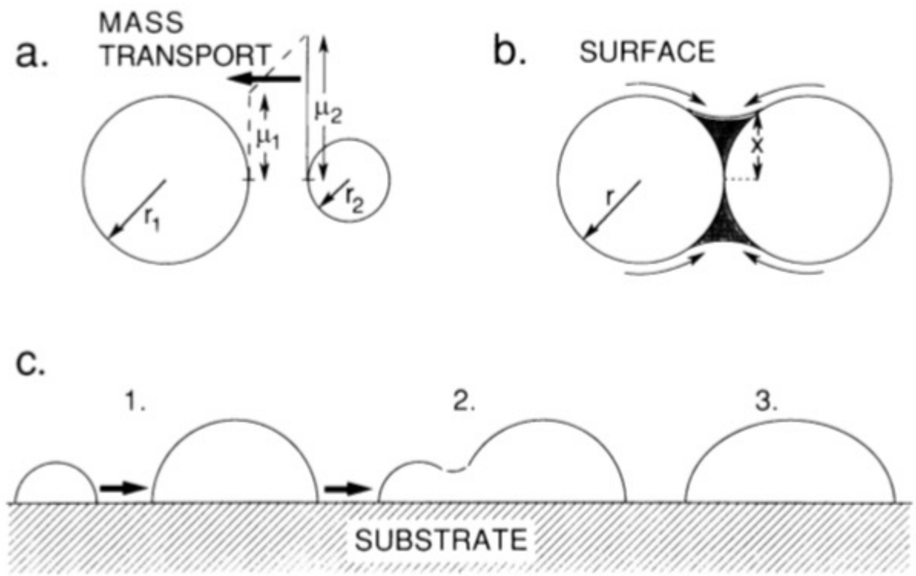
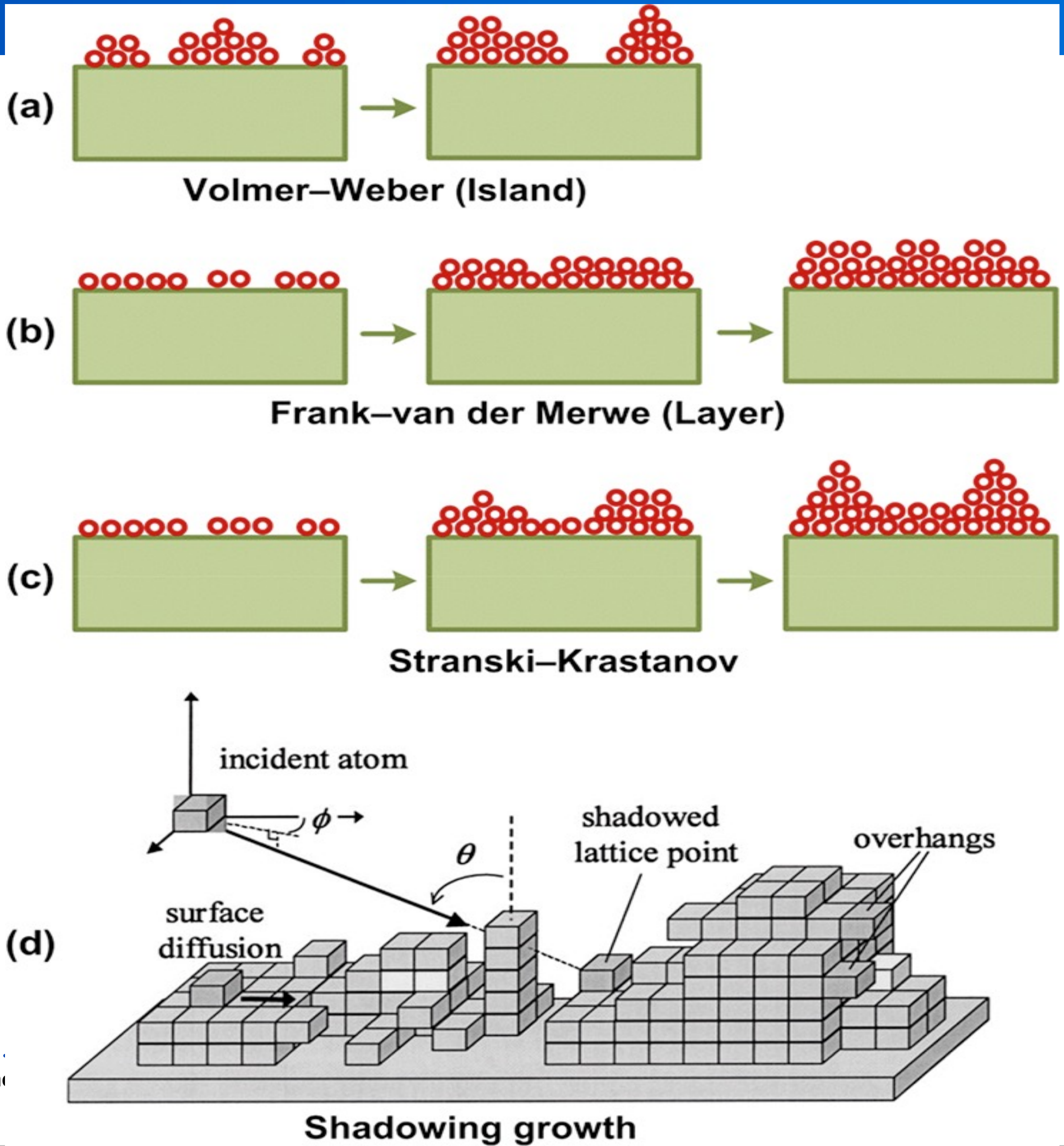


Figure 7-17 Coalescence of islands due to (a) Ostwald ripening, (b) sintering, (c) cluster migration.

M. Ohring, Materials Science of thin films, 2002

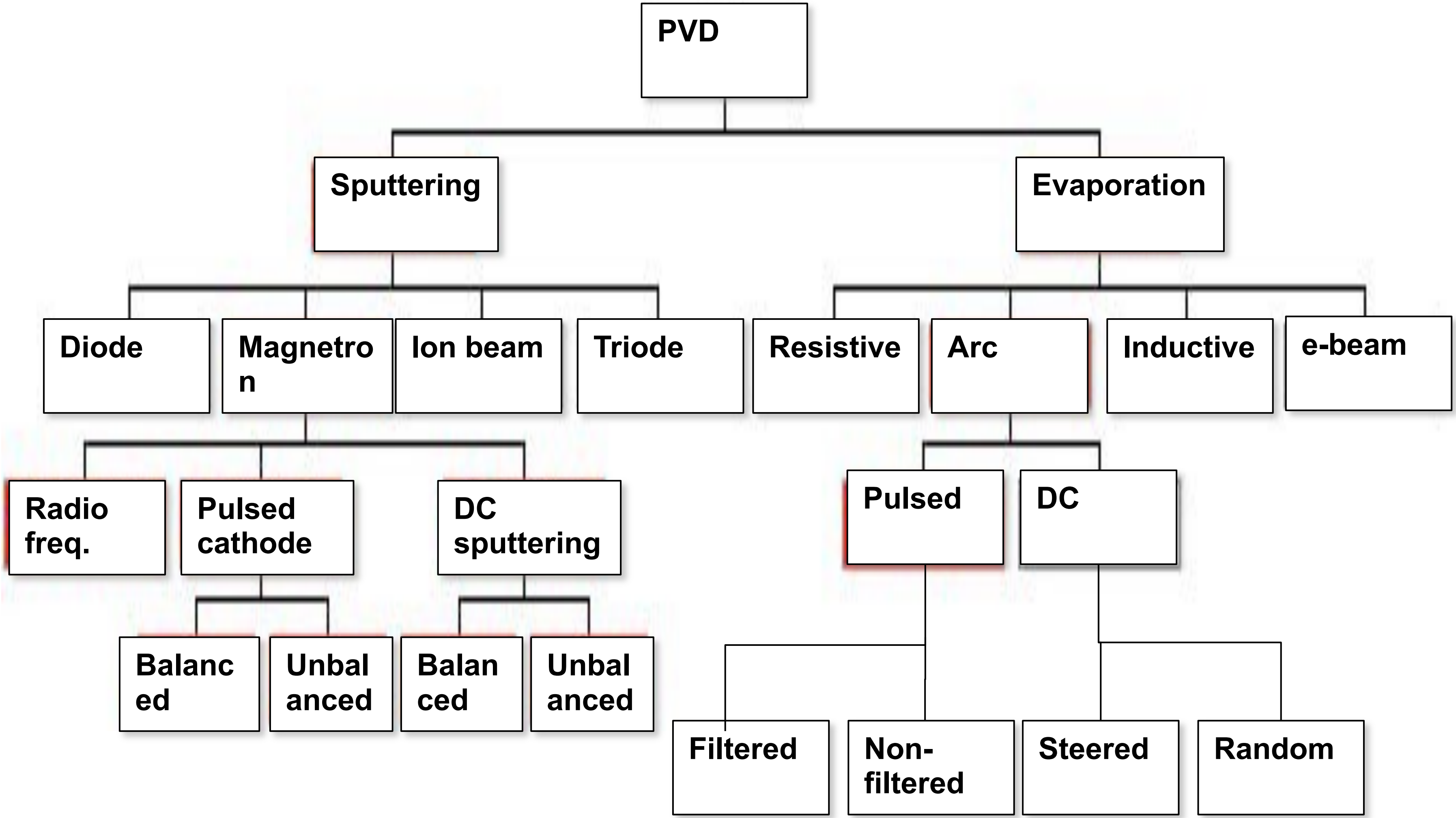
Thin Film growth mechanisms



PVD film growth conditions

- **Thermal atoms land on surface and grow the film**
- **Energetic ions**
  - penetrate some subatomic layers
  - Enhance surface mobility
  - Cause desorption of weakly bond impurity atoms
-

PVD methods



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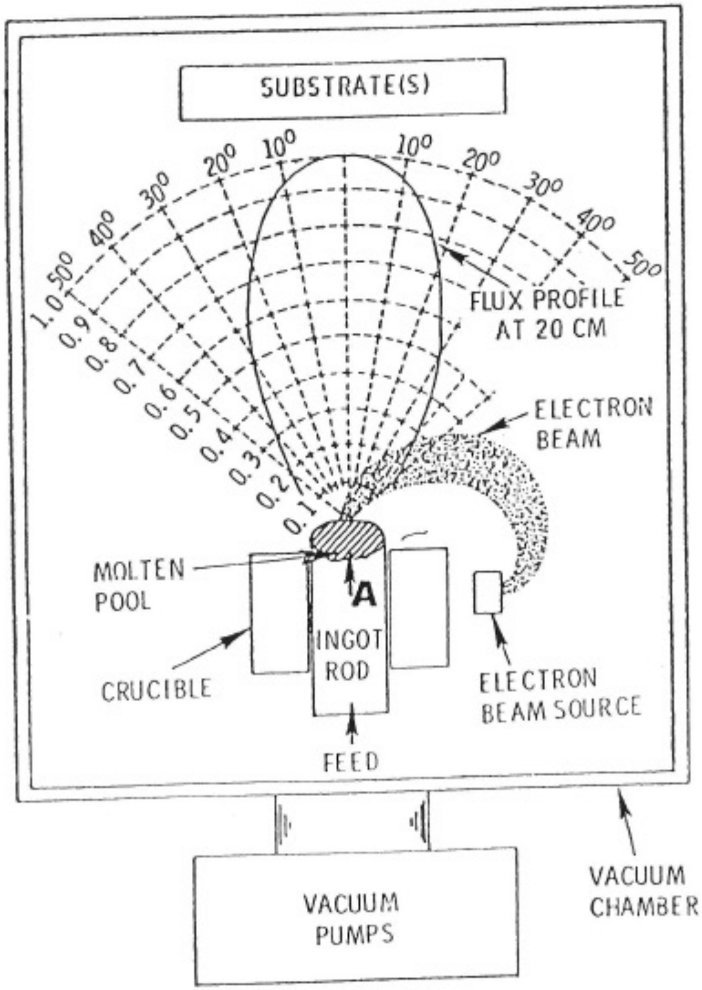
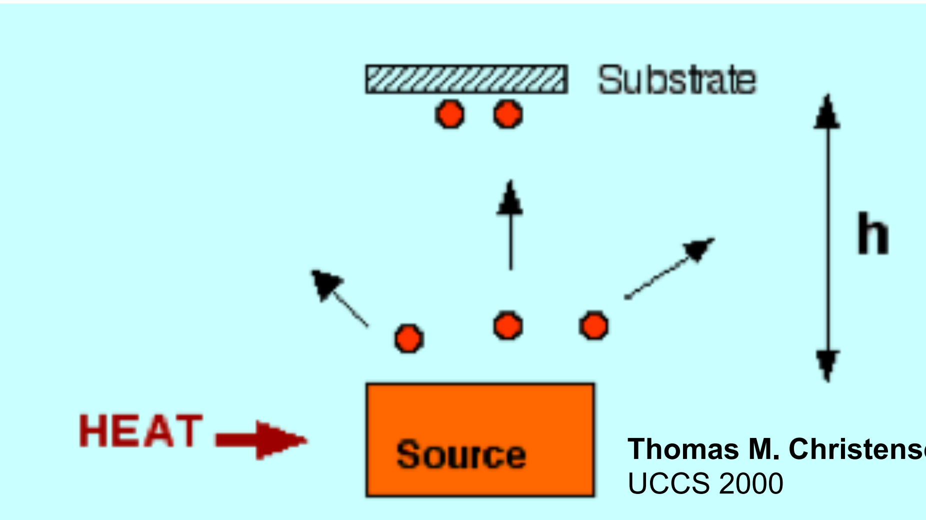
Electron beam evaporation



Evaporation



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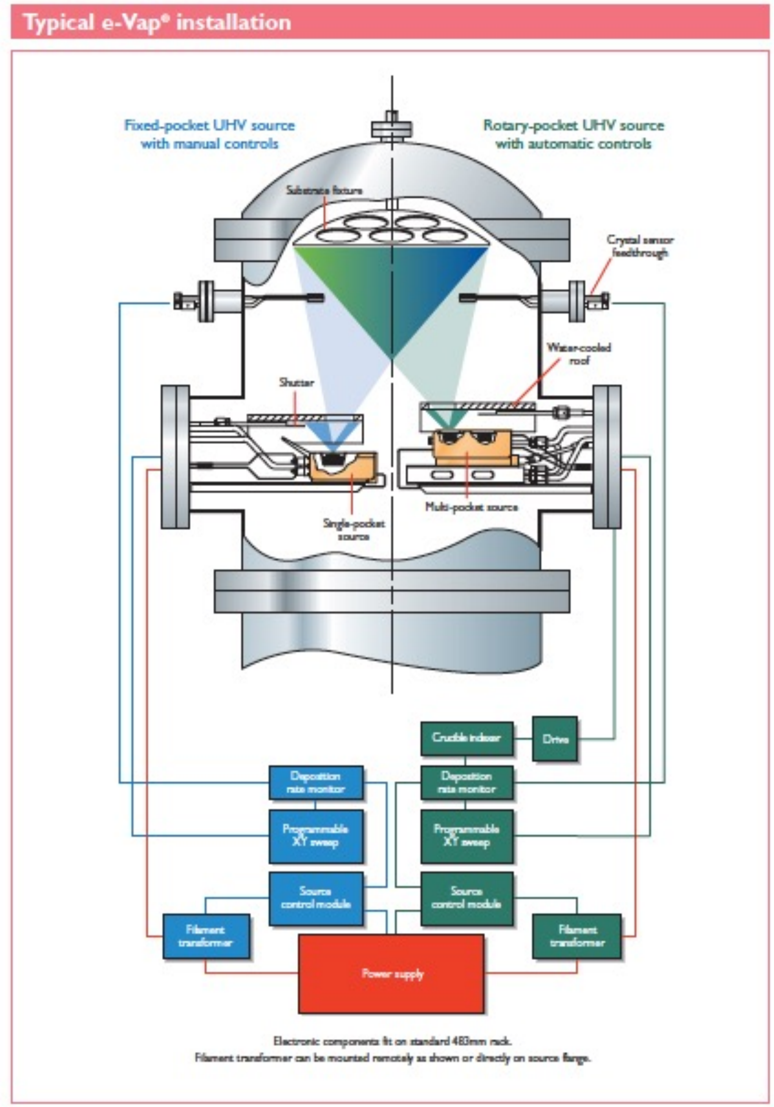
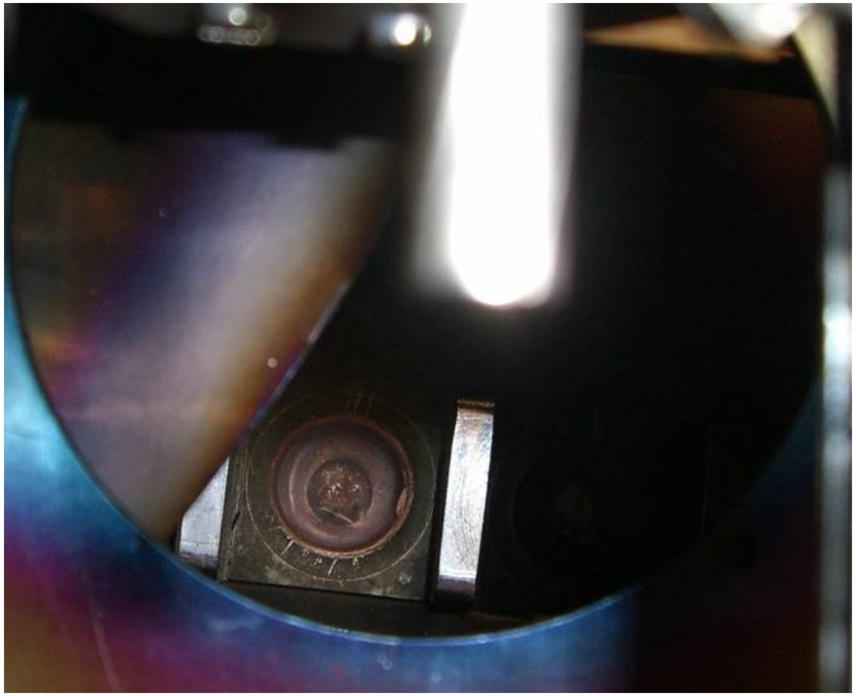
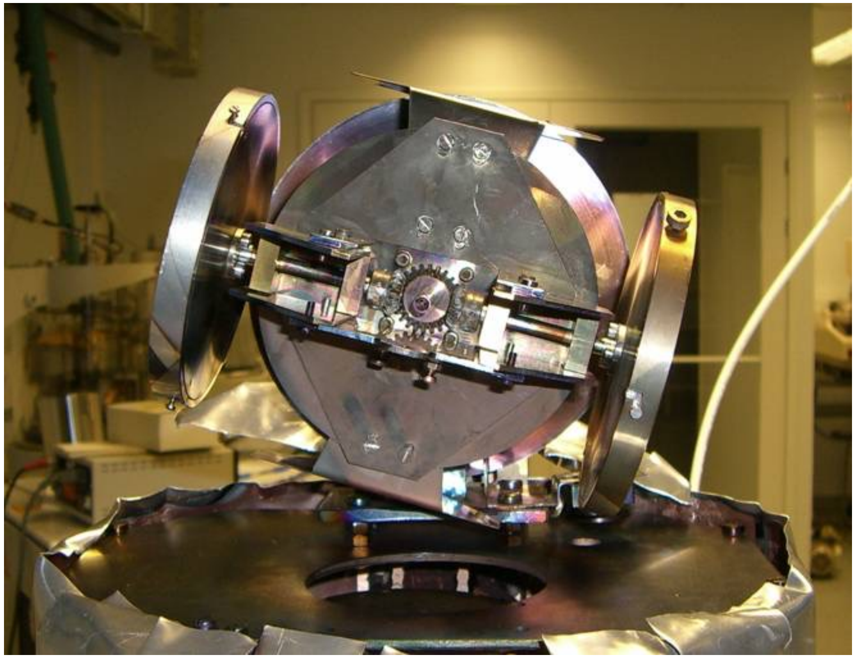
UCCS 2000



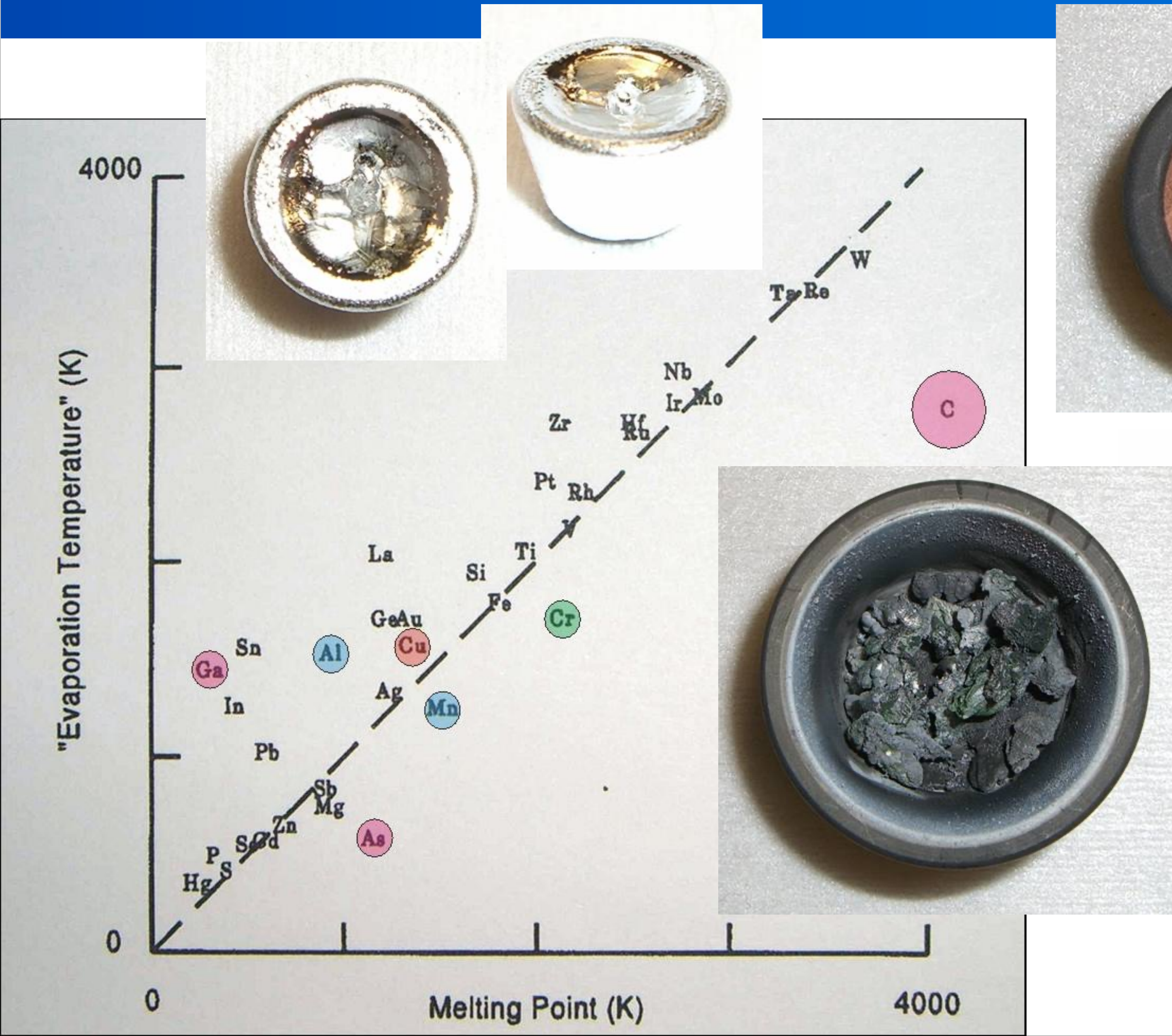
electron beam evaporator

view of sample with beam shutter





Evaporation temperature for p = 10^{-2} torr = $1.3 \cdot 10^{-2}$ mbar



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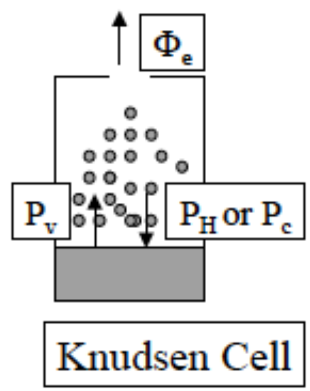
[Mahan, p149]

Vaporization

- **Evaporation or sublimation of atoms from surface due to thermal energy**
- **If the surface of source is in equilibrium with the vapor, the rate of molecules flowing from the source is:**

Coefficient of Evaporation Between 0 and 1

$$\Phi_e = \frac{\alpha_e N_a (P_v - P_h)}{\sqrt{2\pi MRT}}$$



Prof. S. Gleixner, San Jose State University: MatE 270

Vapor pressure

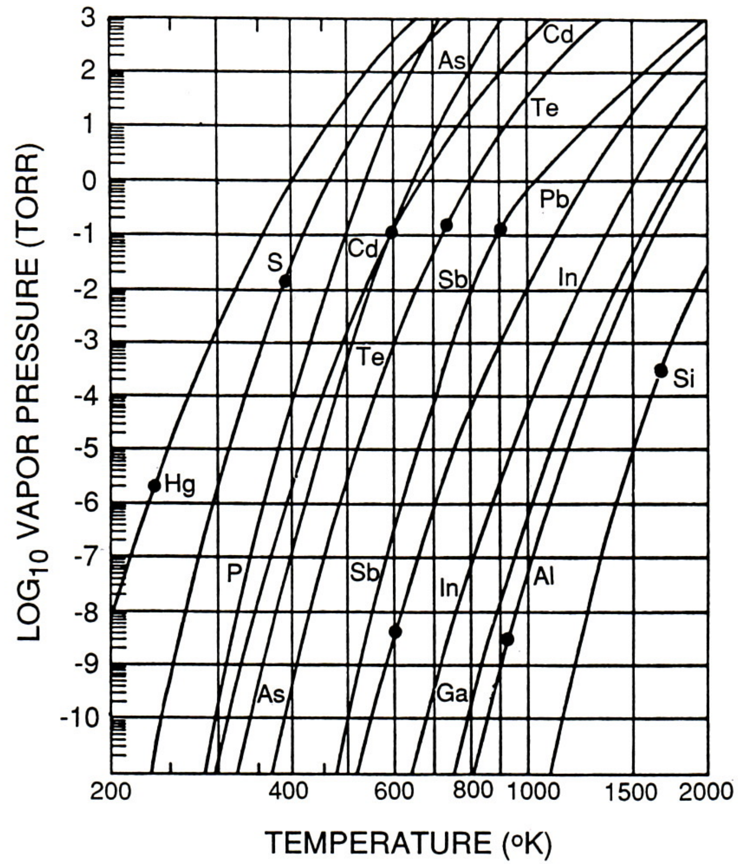


Figure 3-2. Vapor pressures of elements employed in semiconductor materials. Dots correspond to melting points. (Adapted from Ref. 8).

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Vapor pressure

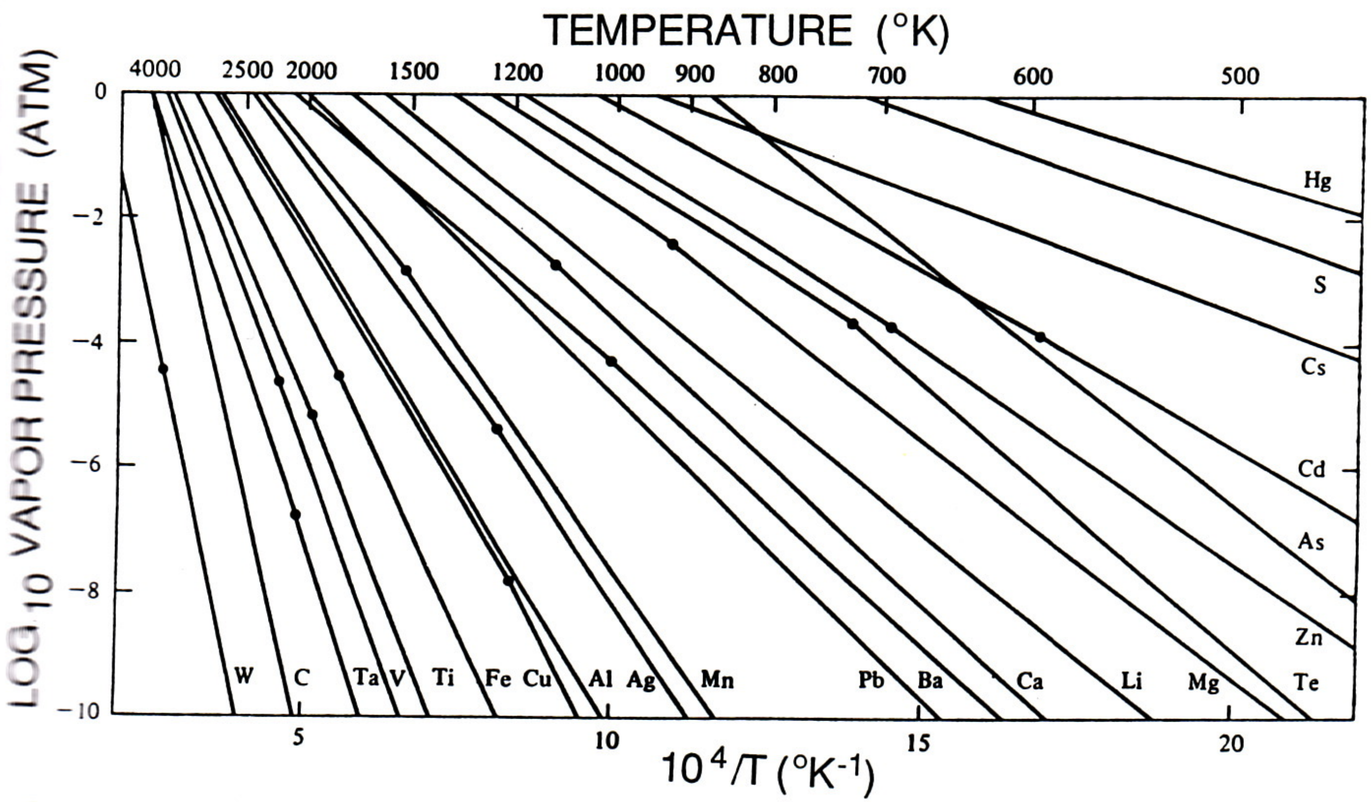

Figure 3-1. Vapor pressures of selected elements. Dots correspond to melting points. (From Ref. 7).

Vapor pressure from tabulations

$$\log(p/atm) = A + B/T + C*\log(T) + D/T^3$$

element	State	A	B	C	D	T(melt) K
'Li'	'solid'	5.667	-8310	0	0	453
'Li'	'liquid'	5.055	-8023	0	0	0
'Na'	'solid'	5.298	-5603	0	0	371
'Na'	'liquid'	4.704	-5377	0	0	0
'K'	'solid'	4.961	-4646	0	0	336
'K'	'liquid'	4.402	-4453	0	0	0
'Rb'	'solid'	4.5857	-4215	0	0	313
'Rb'	'liquid'	4.312	-4040	0	0	0
'Cs'	'solid'	4.711	-3999	0	0	301.6
'Cs'	'liquid'	4.165	-3830	0	0	0
'Be'	'solid'	8.042	-17020	-0.444	0	1560
'Be'	'liquid'	5.786	-15731	0	0	0
'Mg'	'solid'	8.489	-7813	-0.8253	0	923
'Mg'	'liquid'	0	0	0	0	0
'Ca'	'solid'	10.127	-9517	-1.403	0	1112
'Ca'	'liquid'	0	0	0	0	0
'Sr'	'solid'	9.226	-8572	-1.1926	0	1042
'Sr'	'liquid'	0	0	0	0	0

Reference: Alcock, CB< Itkin, VP, and Horrigan MK Canadian Metallurgical Quartely, 23, 309, 1984.

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Vapor pressure of alloys

The complication arises because the different elements do not necessarily have the same vaporization rate (leading to different p_v and Q_e).

$$\frac{\Phi_B}{\Phi_C} = \frac{\gamma_A X_A}{\gamma_B X_B} \frac{P_A(0)}{P_B(0)} \sqrt{\frac{M_B}{M_A}}$$

Prof. S. Gleixner, San Jose State University: MatE 270

Vapor pressure of alloys

Textbook Example

- Want to deposit an Al-2 wt% Cu film from a crucible heated to 1350K
- Therefore want: $\frac{\Phi_{Al}}{\Phi_{Cu}} = \frac{98M_{Cu}}{2M_{Al}}$
- Assuming $\gamma_{Cu}=\gamma_{Al}$
- From Fig 3-1

$$\frac{P_{Al}(0)}{P_{Cu}(0)} = \frac{10^{-3}}{2\times10^{-4}}$$

- So

$$\frac{X_{Al}}{X_{Cu}} = \frac{98\left(2\times10^{-4}\right)\sqrt{63.7}}{2\left(10^{-3}\right)\sqrt{27}} = 15$$

- Need a 15:1 molar ratio of Al to Cu

A!
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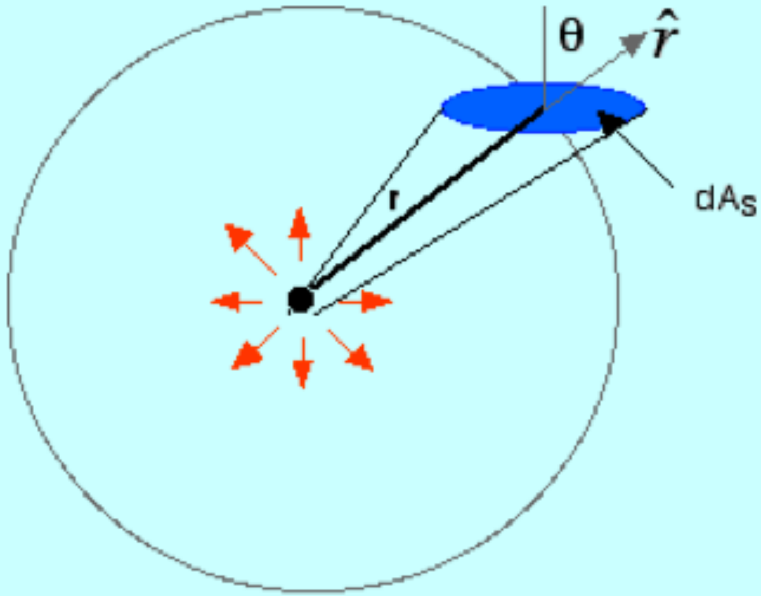
- Point Source



-
  - q = tilt of dA_S from radial direction
  - projection of dA_S onto sphere of radius r = dA_Scosq
  - dM_S = mass hitting dA_S
  - M_e = total evaporated mass
- $$\frac{dM_S}{M_e} = \frac{dA_S \cos\theta}{4\pi r^2}$$

$$\frac{dM_S}{dA_S} = \frac{M_e \cos\theta}{4\pi r^2}$$

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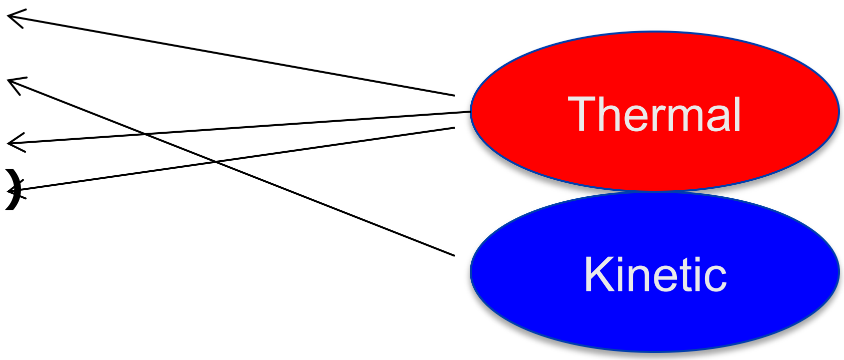
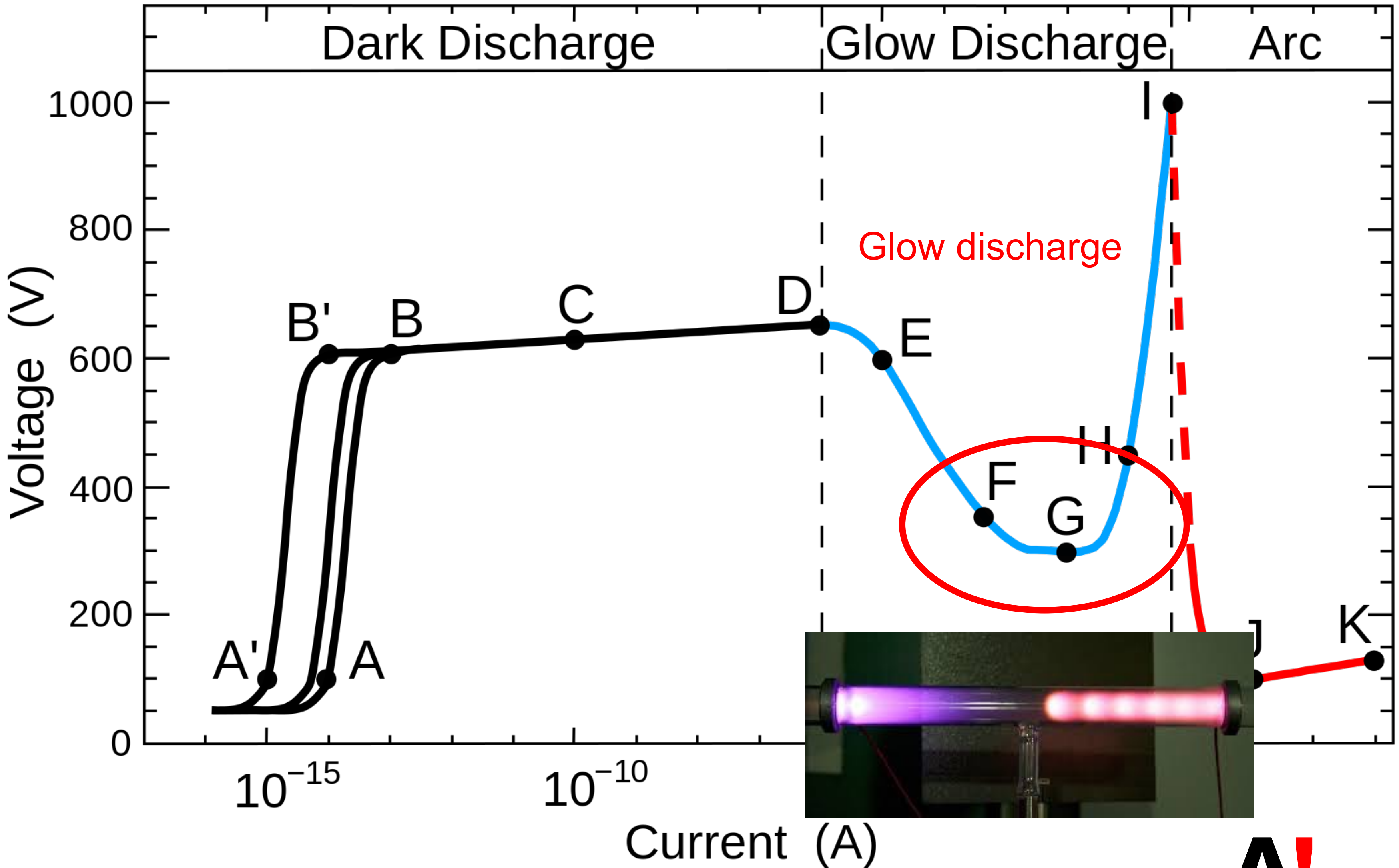
Extraction of materials from solid

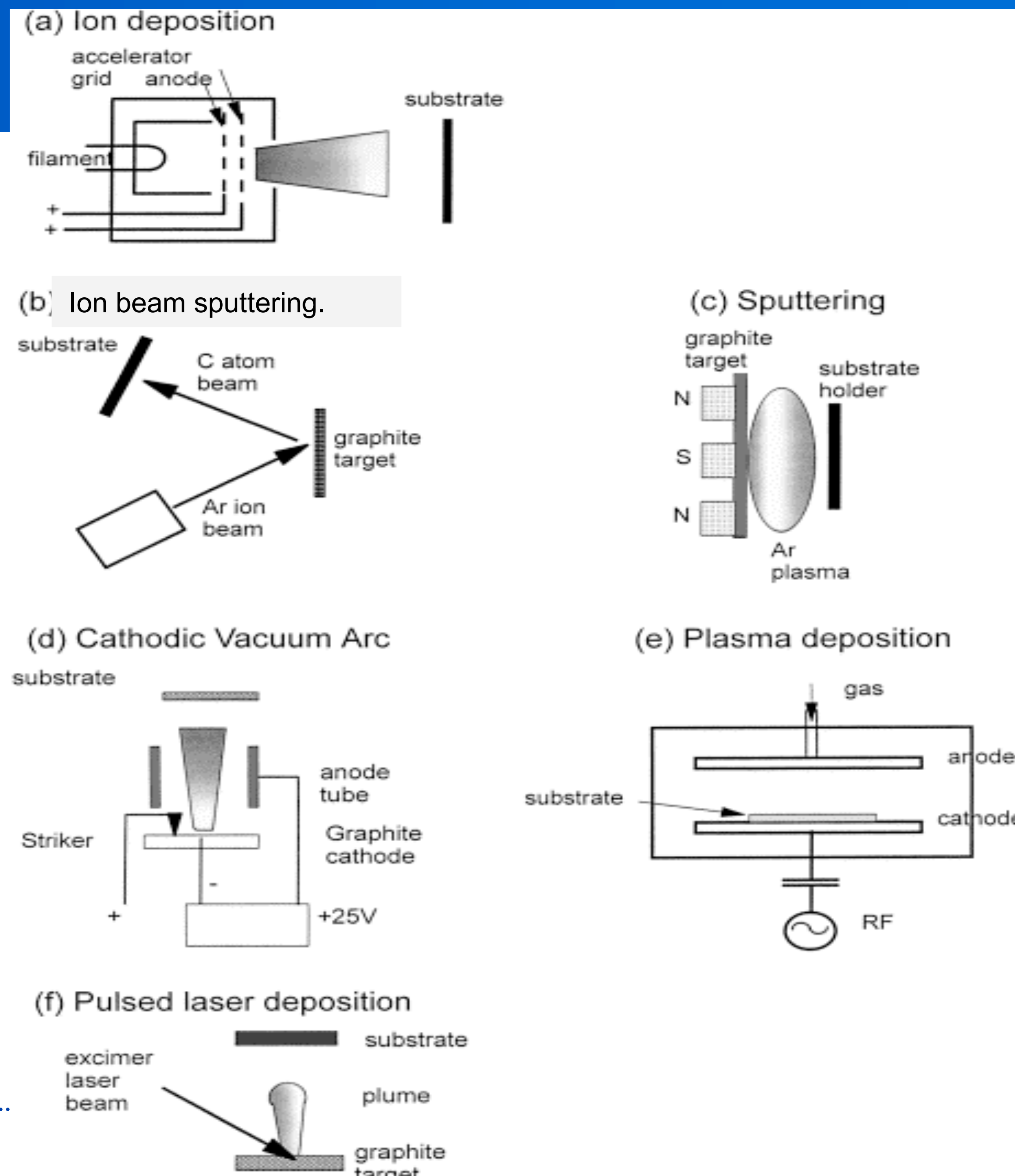
- **Evaporation**
- **Sputtering**
- **Arc (evaporation)**
- **Laser heating**



DC Plasma glow discharge and arc

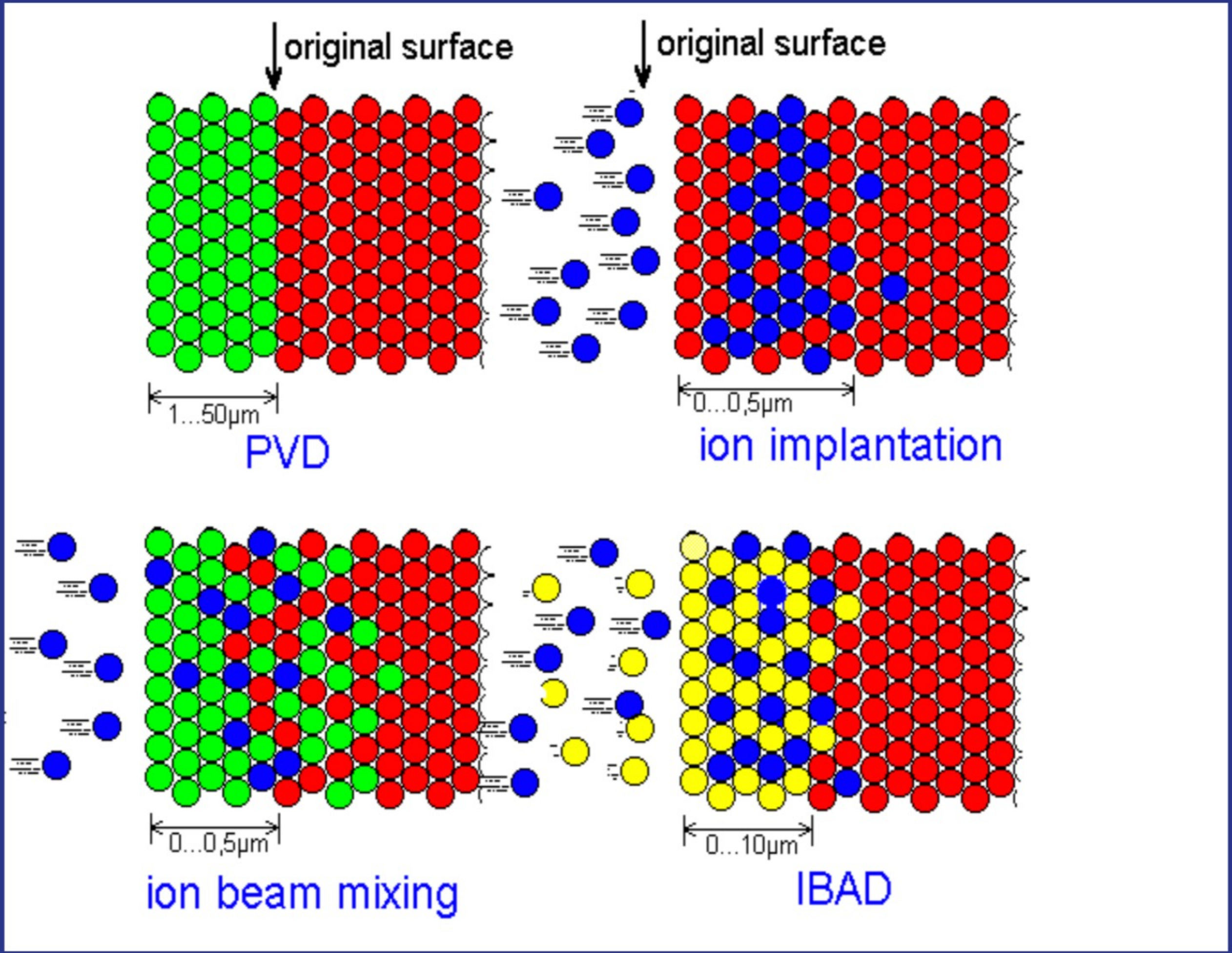


PVD methods

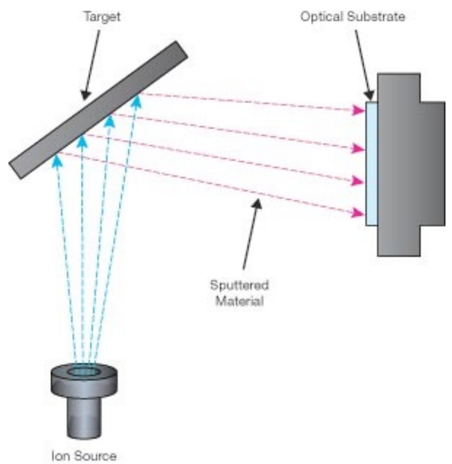

(a) Ion deposition
accelerator grid
anode
substrate
filament
+
+
(b) Ion beam sputtering.
substrate
C atom beam
graphite target
Ar ion beam
(c) Sputtering
graphite target
substrate holder
N
S
N
Ar plasma
(d) Cathodic Vacuum Arc
substrate
anode tube
Striker
Graphite cathode
-
+
+25V
(e) Plasma deposition
gas
anode
substrate
cathode
RF
(f) Pulsed laser deposition
substrate
excimer laser beam
plume
graphite target

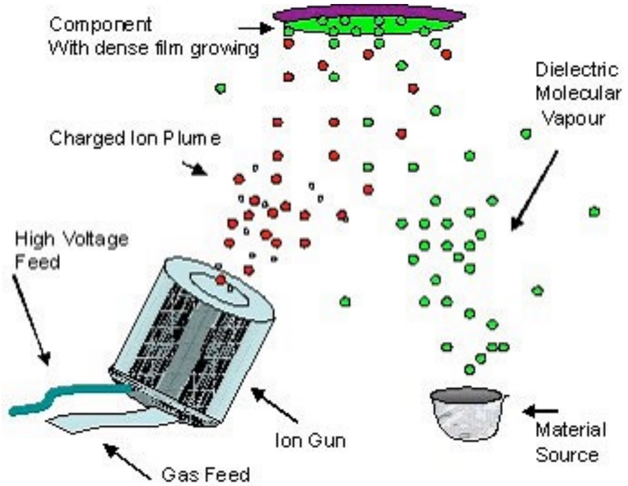
PVD and Ion Assisted Processes

Which role can energetic ions play

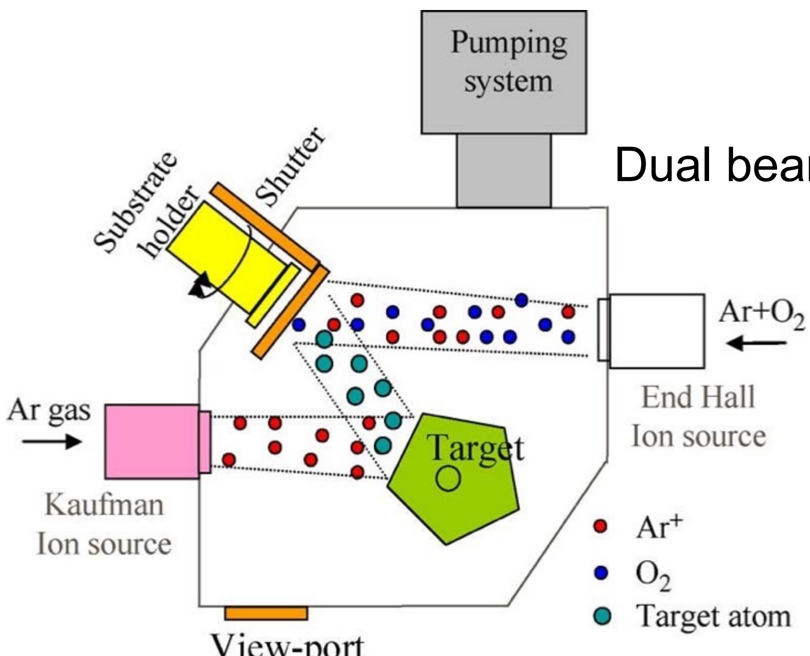


Ion beam sputtering

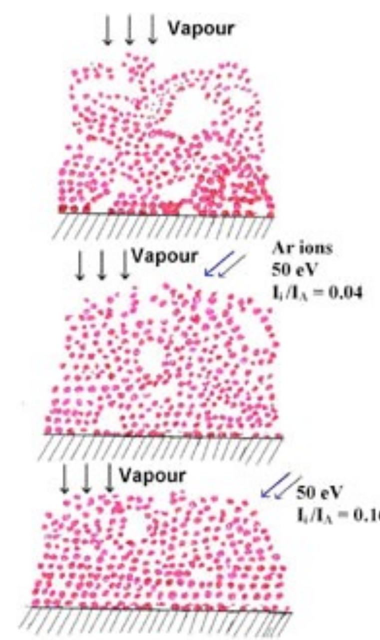




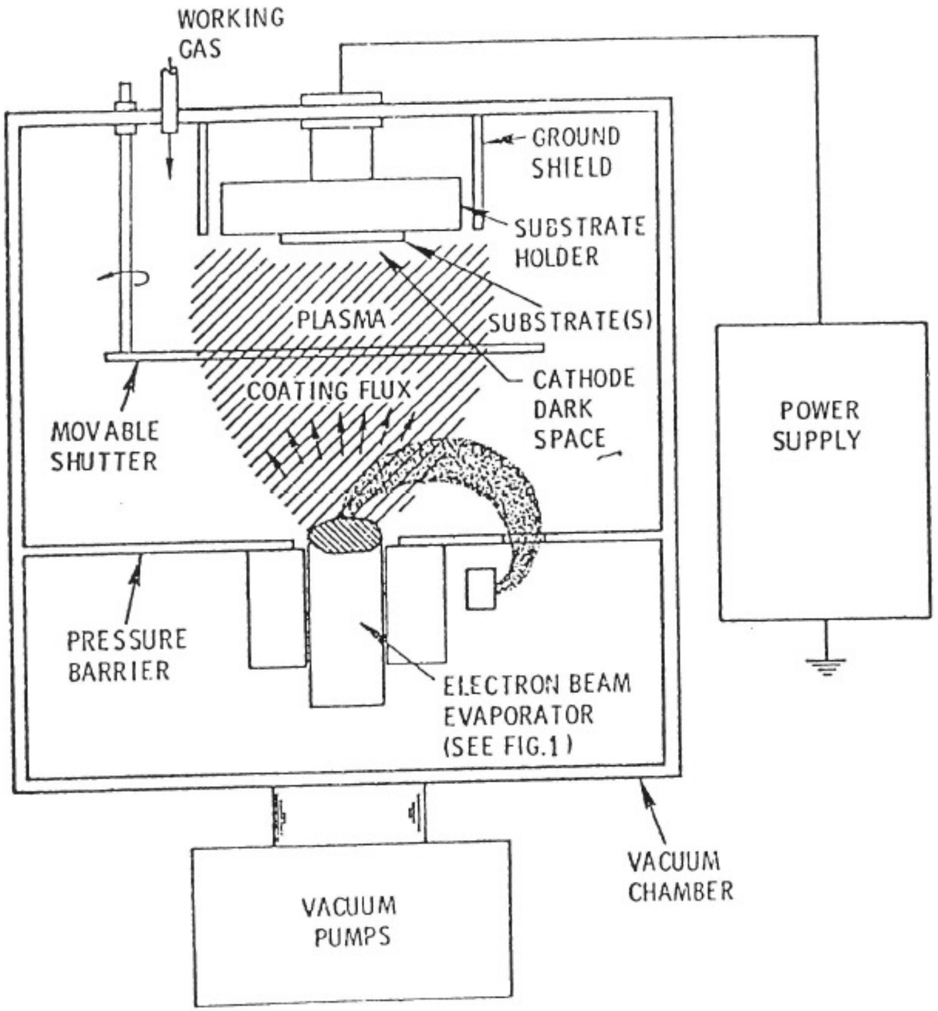
Kaufman
http://www.youtube.com/watch?v=Ibcr-B258J8&NR=1



Dual beam sputtering



Ion plating



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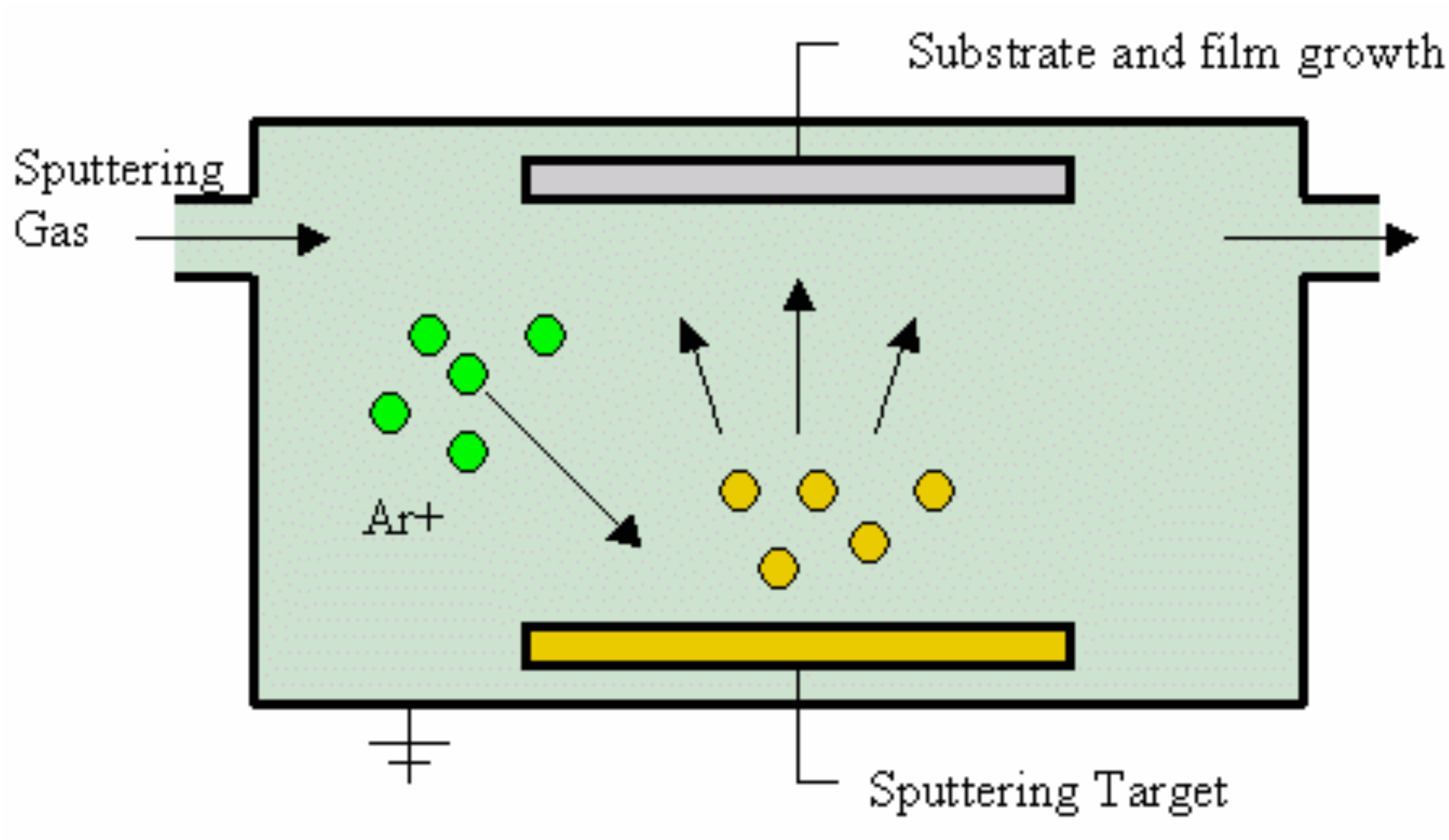
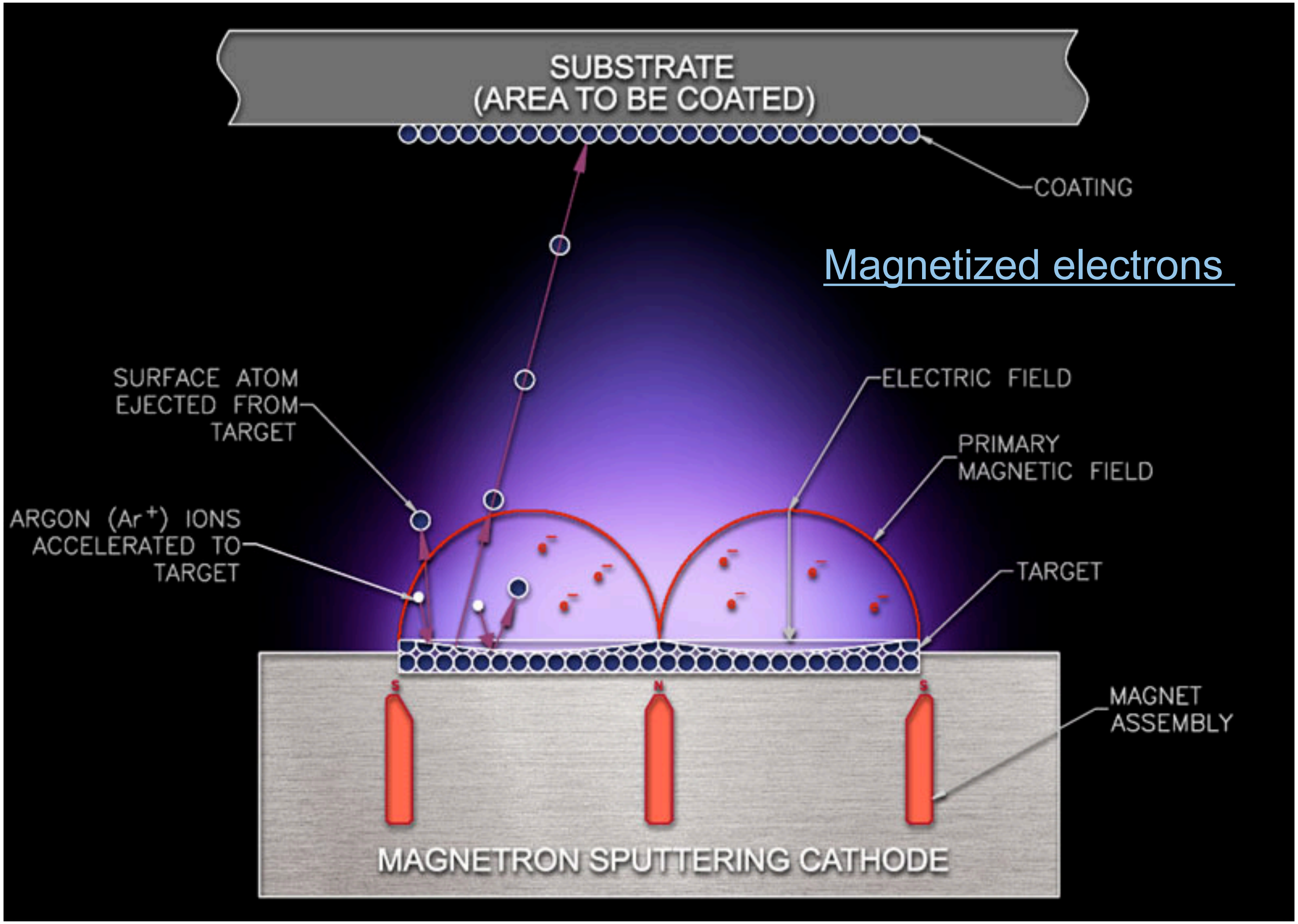
Sputtering



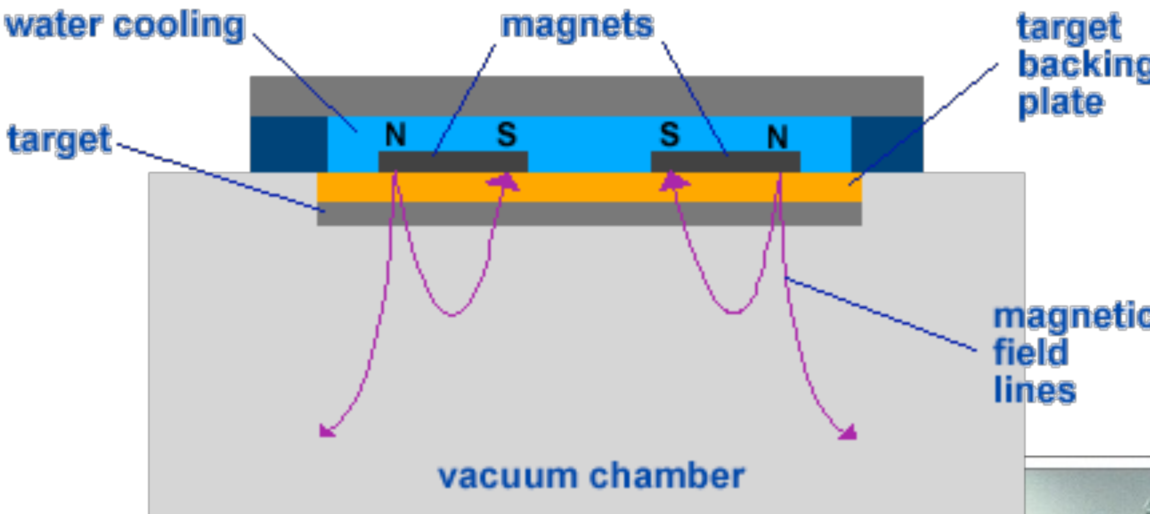
Substrate and film growth
Sputtering
Gas
Ar+
Sputtering Target

Magnetron-sputtering

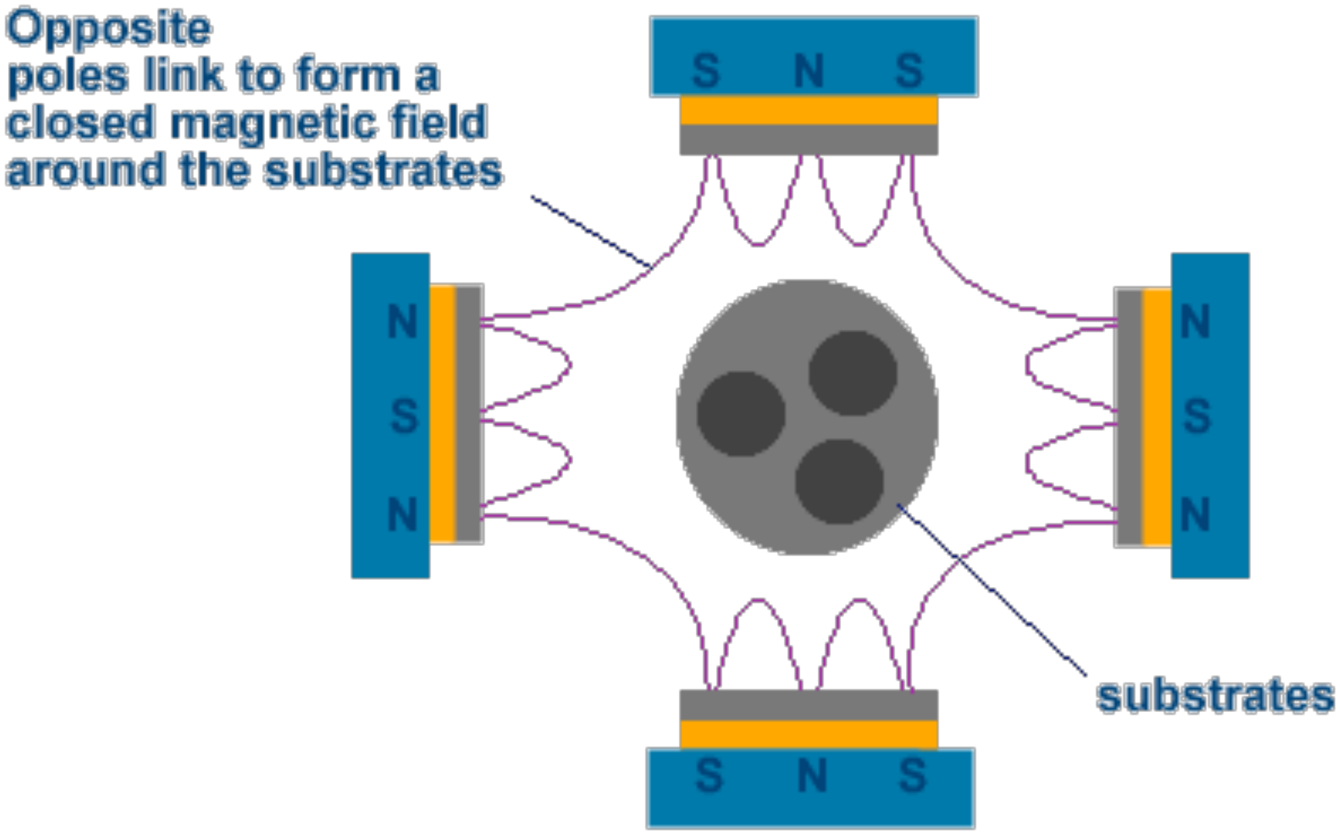


Lähde: Angstrom Sciences, Inc.

Unbalanced magnetron sputtering



Closed field magnetron sputtering




TECH
COATINGS
LIMITED

Magnetron Sputtering video

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Surface coating methods – more details

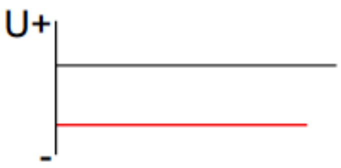
Table 2.1. Comparative typical characteristics of some of the main coating methods.

	Gaseous State Processes					Solution Processes		Molten or Semi-Molten State Processes		
	PVD	PAPVD	CVD	PACVD	Ion Implantation	Sol-Gel	Electro-Plating	Laser	Thermal Spraying	Welding
Deposition rate (kg/h)	Up to 0.5 per source	Up to 0.2	Up to 1	Up to 0.5		0.1–0.5	0.1–0.5	0.1–1	0.1–10	3.0–50
Coating thickness or treatment depth (μm)	0.1–1000	0.1–100	0.5–2000	1–20	0.01–0.5	1–10	10–500	50–2000	50–1000	1000–10,000
Component size		Limited by chamber size				Limited by solution bath		May be limited by chamber size		
Substrate deposition or treatment temperature (°C)	50–500	25–500	150–12,000	150–700	50–200	25–1000	25–100	200–2000	100–800	500–1200
Substrate material	Metals, ceramics, polymers	Metals, ceramics	Metals, ceramics	Metals, ceramics	Metals, ceramics, polymers	Metals, ceramics, polymers	Metals, ceramics, polymers	Metals		
Pretreatment	Mechanical/ chemical	Mechanical/ chemical plus ion bombardment	Mechanical/ chemical	Mechanical/ chemical plus ion bombardment	Chemical plus ion bombardment	Grit blast and/or chemical clean	Chemical cleaning and etching	Mechanical and chemical cleaning		
Post-treatment	None	None	Substrate stress relief	None	None	High temperature	None/thermal treatment	None/substrate stress relief		None
Uniformity of coating	Good	Good	Very good	Good	Line of sight	Fair/good	Fair/good	Fair	Variable	Variable
Bonding mechanism	Atomic	Atomic plus diffusion	Atomic	Atomic plus diffusion	Integral	Surface forces		Mechanical/ chemical/ metallurgical		

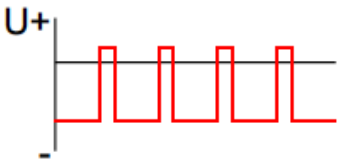
PULSED SPUTTERING

Definitions

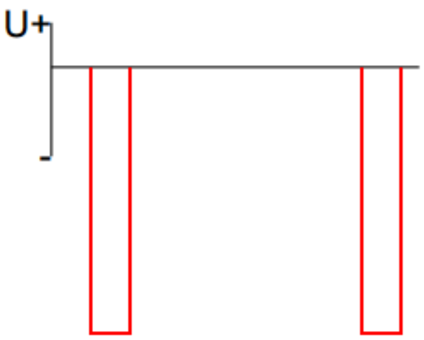
- DC-sputtering



- Pulsed DC



- HiPIMS



High power pulsed Magnetron Sputtering

High Power Pulsed Magnetron Sputtering (HPPMS)

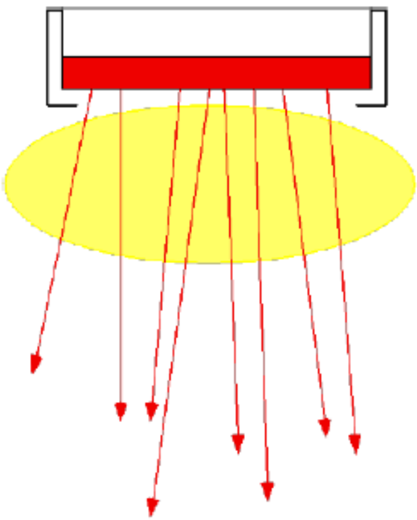
- Introduced by Kouznetsov et al.*
  - Also known as HIPIMS – High Power Impulse Magnetron Sputtering
- High power pulses of short duration
  - Peak value typically 100 times greater than conventional magnetron sputtering
    - Peak power densities of 1-3 kW/cm^2
  - Pulse width of 100 - 150 μsec
  - Discharge voltages of 500-1000 V

*V. Kouznetsov, K. Macák, J. M. Schneider, U. Helmersson, and I. Petrov, "A Novel Pulsed Magnetron Sputter Technique Utilizing Very High Target Power Densities," Surf. Coat. Technol. 122 (1999) 290.

What is HiPIMS?

High peak powers (500-2000 W/cm^2)
Reasonable average powers
Low duty factors (0.5 – 5 %)

Plasma densities in the range of 10^{19} m^{-3}
(Normal magnetron sputtering 10^{16} m^{-3})

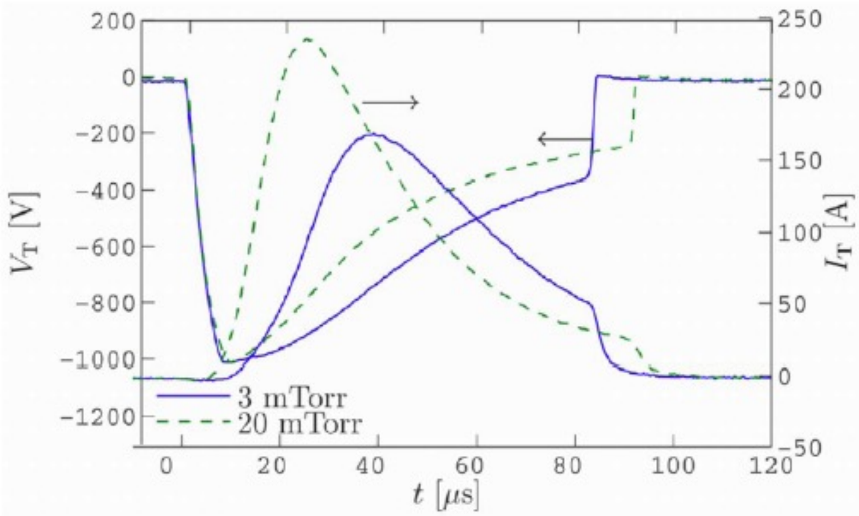


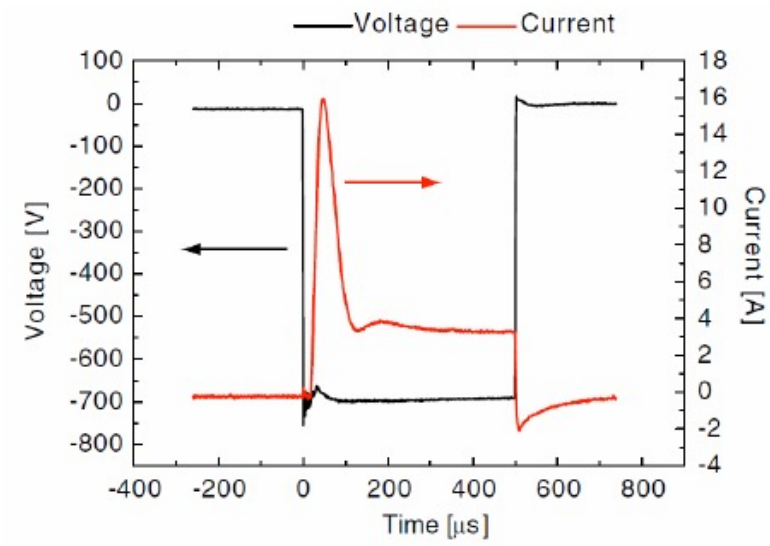
D.V. Mozgrin, I.K. Fetisov, and G.V. Khodachenko, Plasma Phys. Rep. **21,** 400 (1995)

S.P. Bugaev, N.N. Koval, N.S. Sochugov, and A.N. Zakharov, Proceedings of the XVIIth International Symposium on Discharges and Electrical Insulation in Vacuum, July 21-26, 1996, Berkeley, CA, USA, vol., p.1074

V. Kouznetsov, K. Macák, J.M. Schneider, U. Helmersson, and I. Petrov, Surf. Coat. Technol. **122**, 290 (1999)

Typical HiPIMS pulses

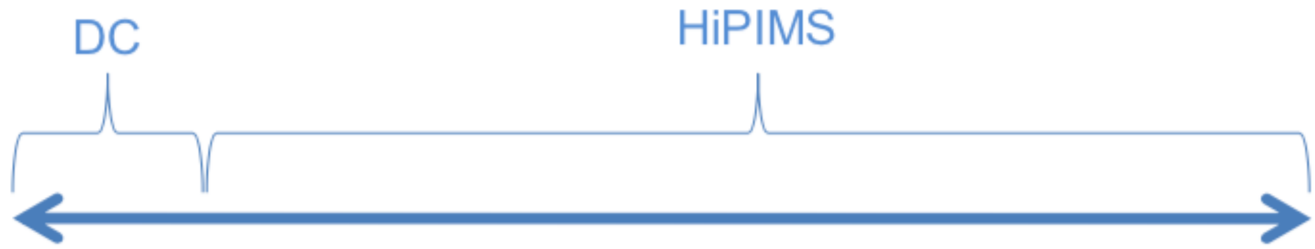




J.T. Gudmundsson, P. Sigurjonsson, P. Larsson, D. Lundin, U. Helmersson, J. Appl. Phys. **105**, 123302 (2009)

D. Lundin, N. Brenning, D. Jädernäs, P. Larsson, E. Wallin, M. Lattemann, M.A. Raadu and U. Helmersson, Plasma Sources Sci. Technol. **18**, 045008 (2009).

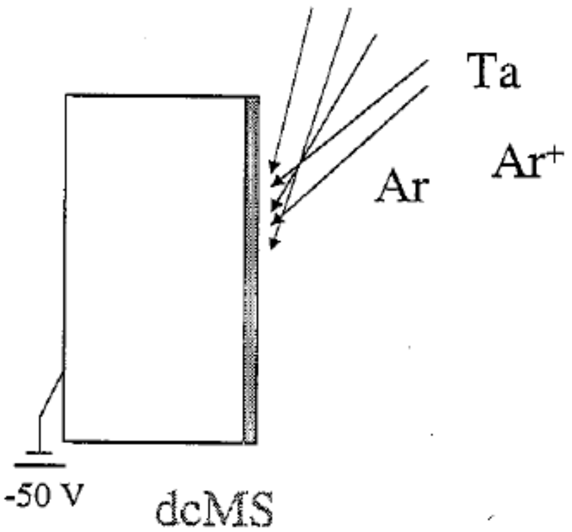
DC - HiPIMS

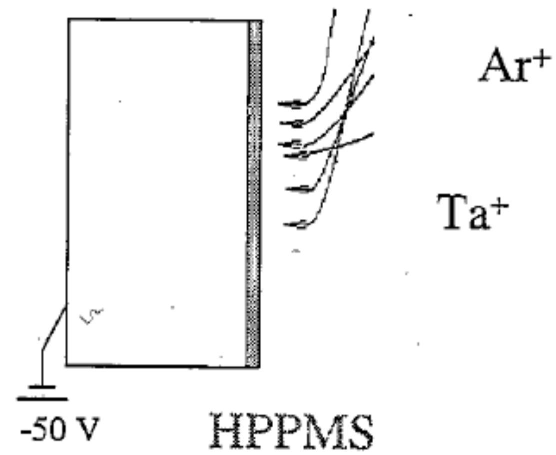


No ionization of the sputtered material

Full ionization of the sputtered material

DC-MS and HIPIMS Deposition



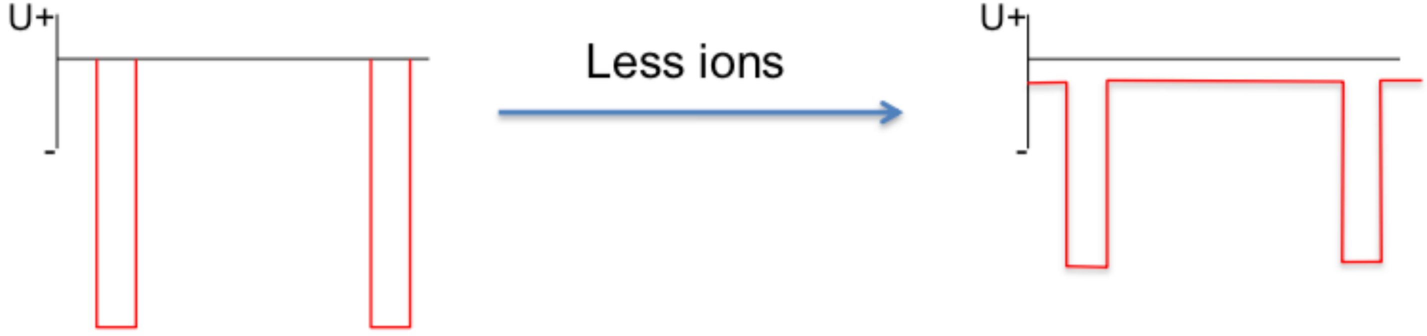


- Shadowing effect
- Bombardment of surface with Ar ions

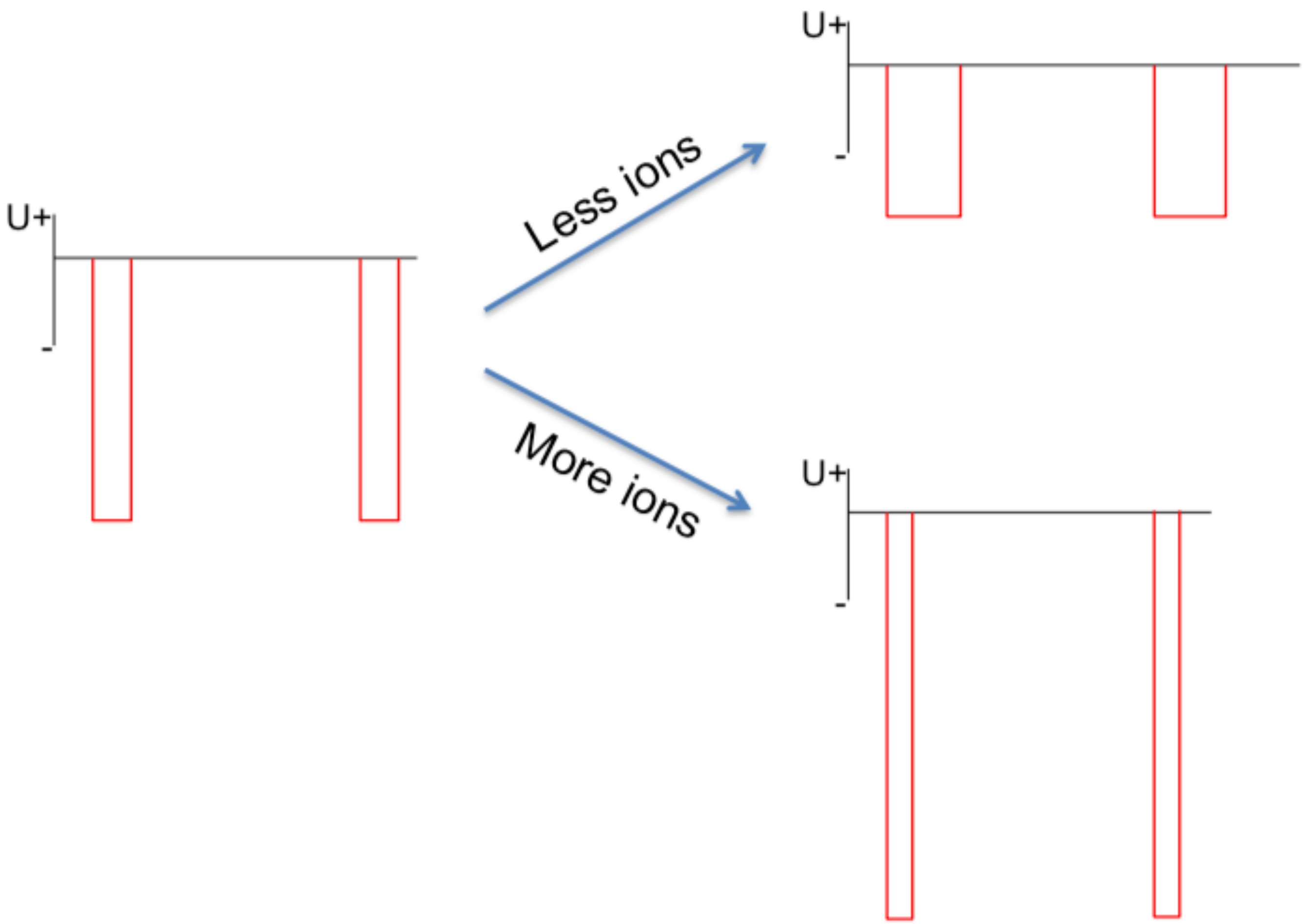
- Efficient momentum transfer (Metal ion bombardment)
- Enhanced surface diffusion

*J. Alami, P. O. A. Persson, D. Music, J. T. Gudmundsson, J. Bohlmark, and U. Helmersson, "Ion-assisted physical vapor deposition for enhanced film properties on nonflat surfaces," J. Vac. Sci. Technol. A 23(2) (2005) 278.

How to tune the “degree of HiPIMS”?



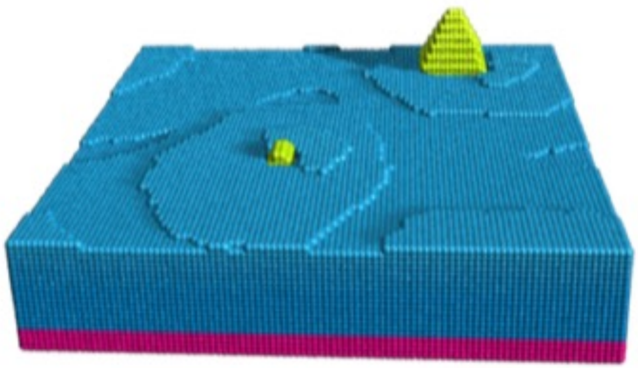
How to tune the "degree of HiPIMS"?

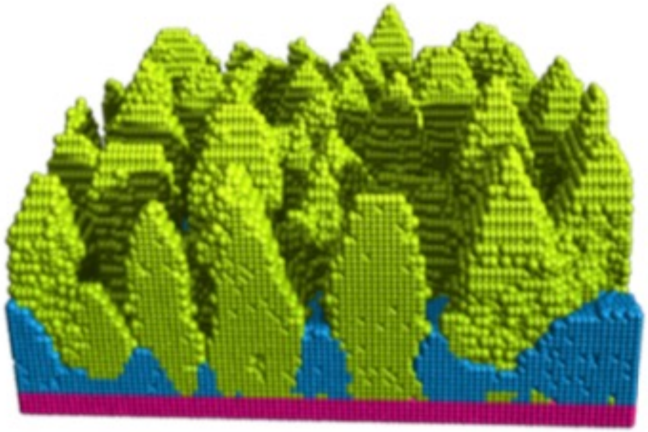


Film quality

High adatom mobility:
001-texture

Low adatom mobility:
111-texture



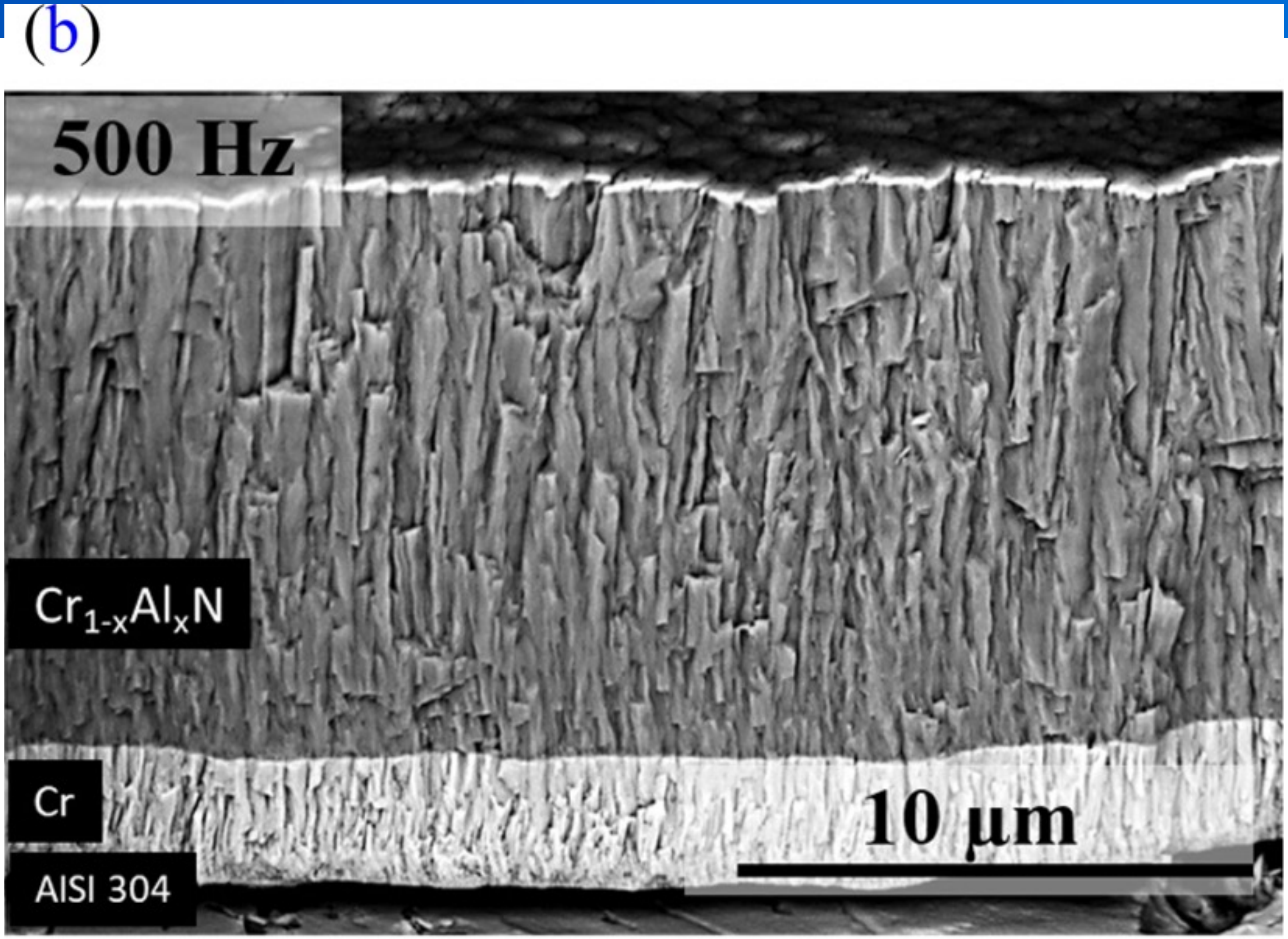


F. H. Baumann, D. L. Chopp, T. Díaz de la Rubia, G. H. Gilmer, J. E. Greene, H. Huang, S. Kodambaka, P. O'Sullivan, and I. Petrov, *MRS Bulletin,* 26 182 (2001)

HIPIMS Summary

- HiPIMS is here to stay!
- Deposition rate is often **not** an issue. Focus on film performance!
- General achievements:
  - Lower growth temperatures
  - Denser films
  - More stable reactive processes
  - Higher film adhesion
  - Better film coverage on complex shaped substrates

HIPIMS denser films



Nature. Scientific RepoRtS |
(2019) 9:15898 | https://doi.org/10.1038/s41598-019-52226-1

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HPPMS denser films

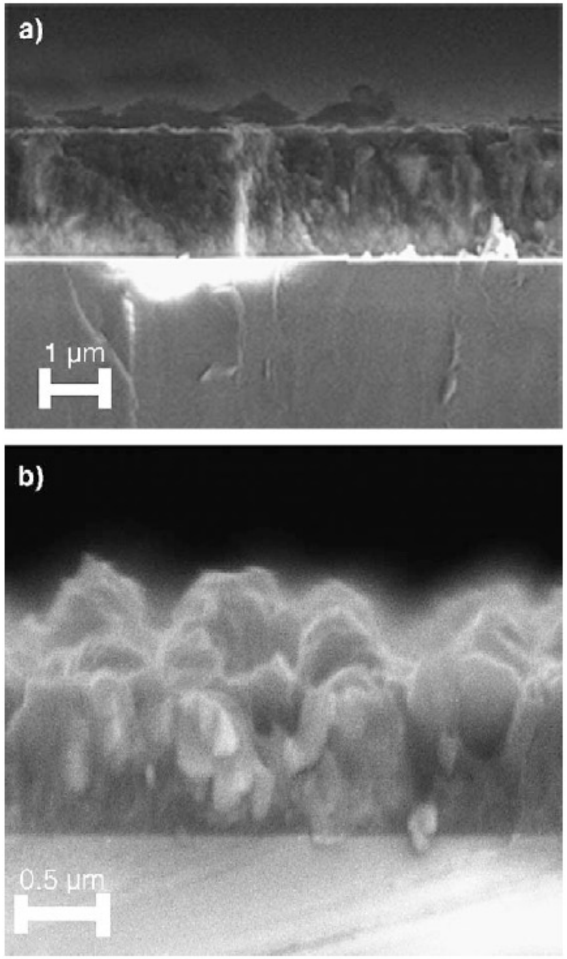
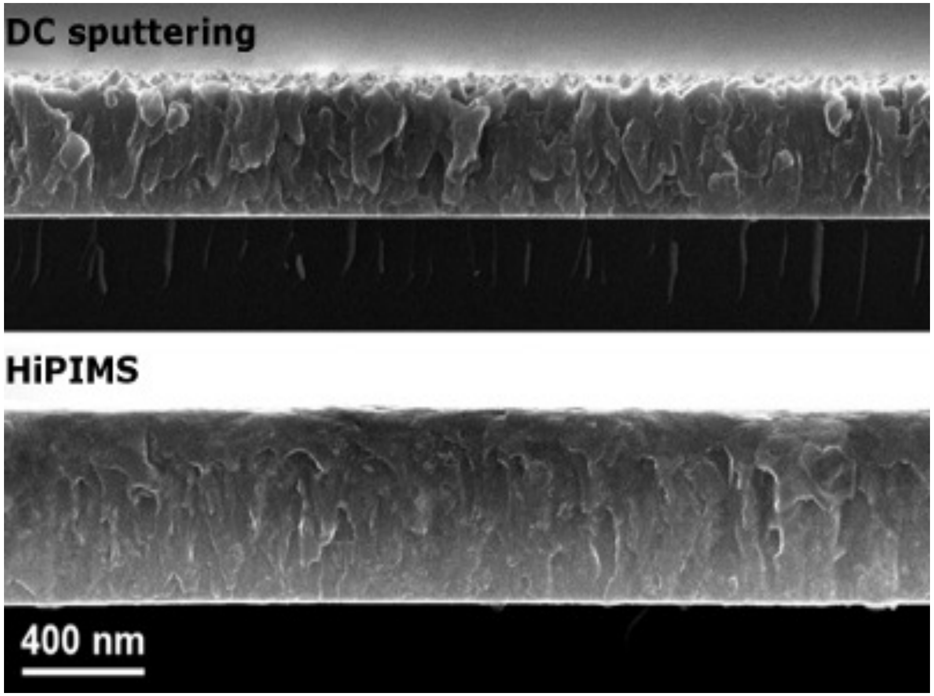


Fig. 2. SEM micrographs from Ti–Si–C films grown facing the target surface by HIPIMS (a) and dcMS (b), using 20 mTorr Ar, a sputtering gas and a substrate bias of −20 V.



Ti sputtered by DC magnetron and HPPMS. Note the difference in film density and smooth top surface of HPPMS film

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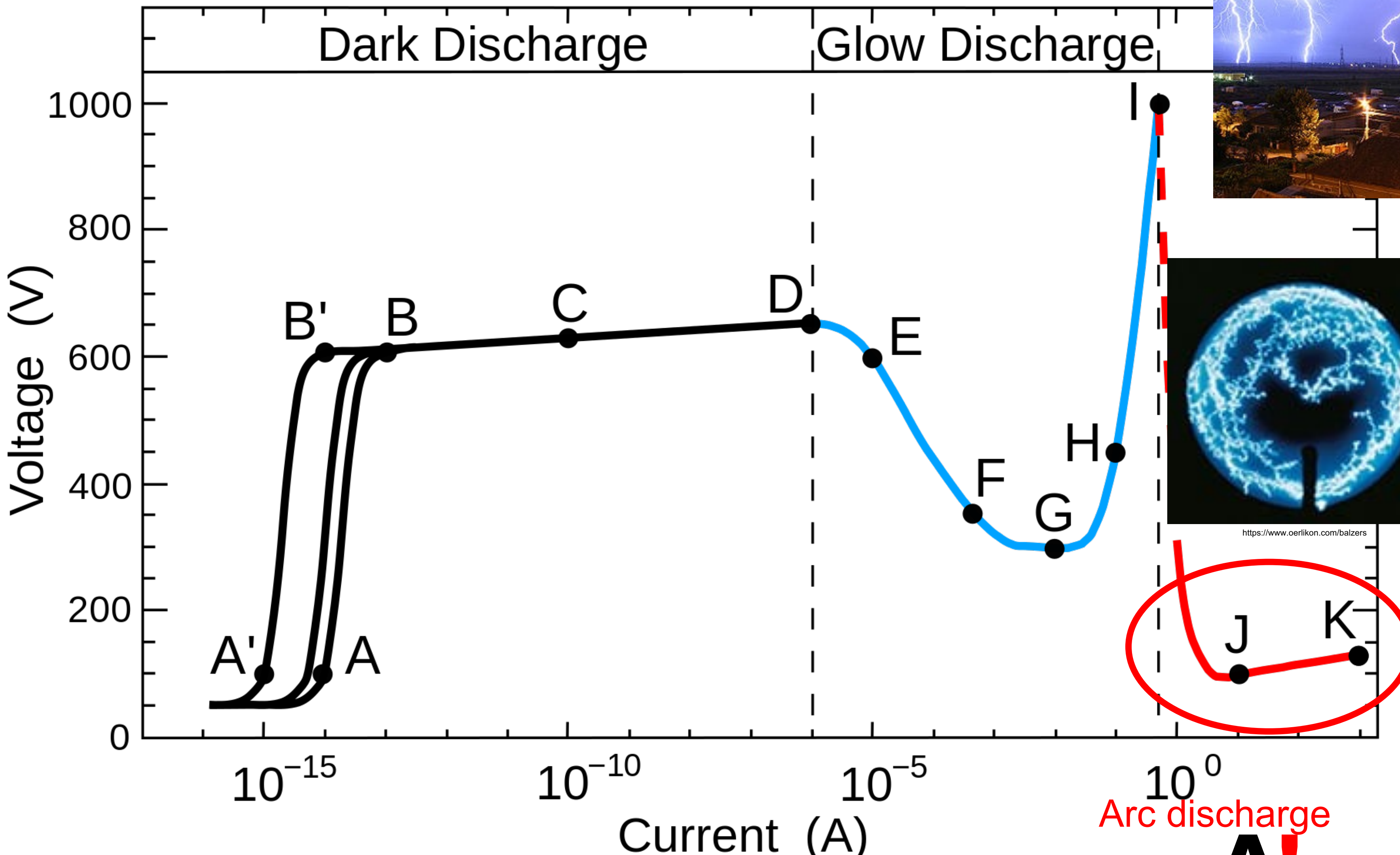
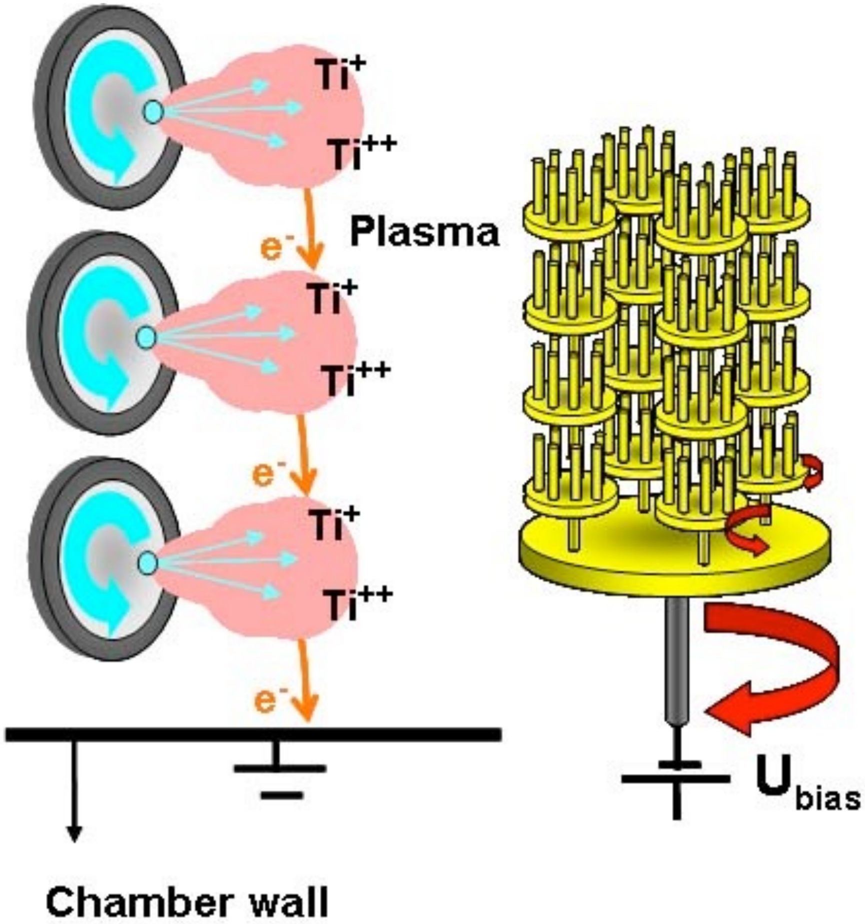
DC Plasma glow discharge and arc



Arc discharge deposition



Cathodic arc spot evolution

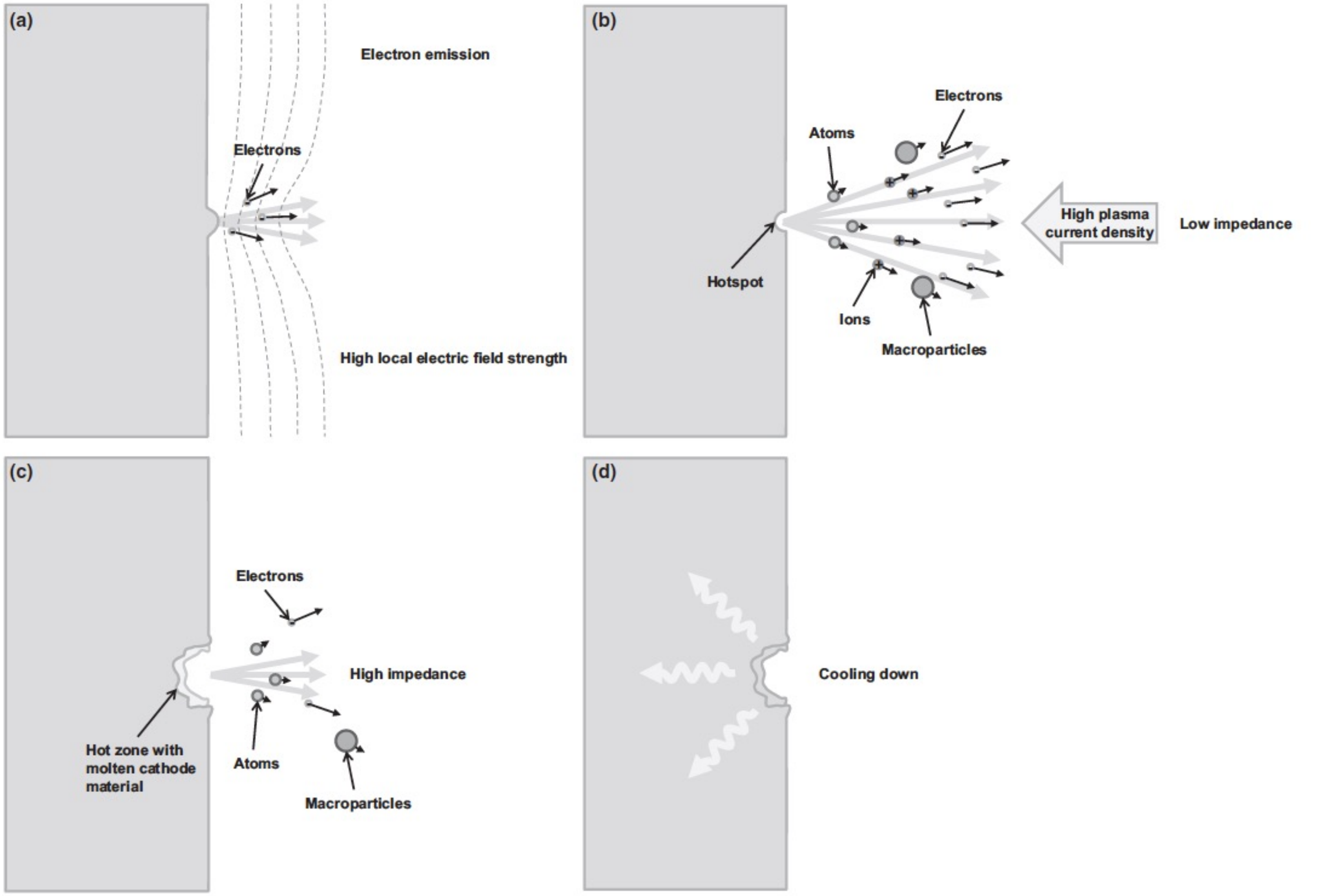
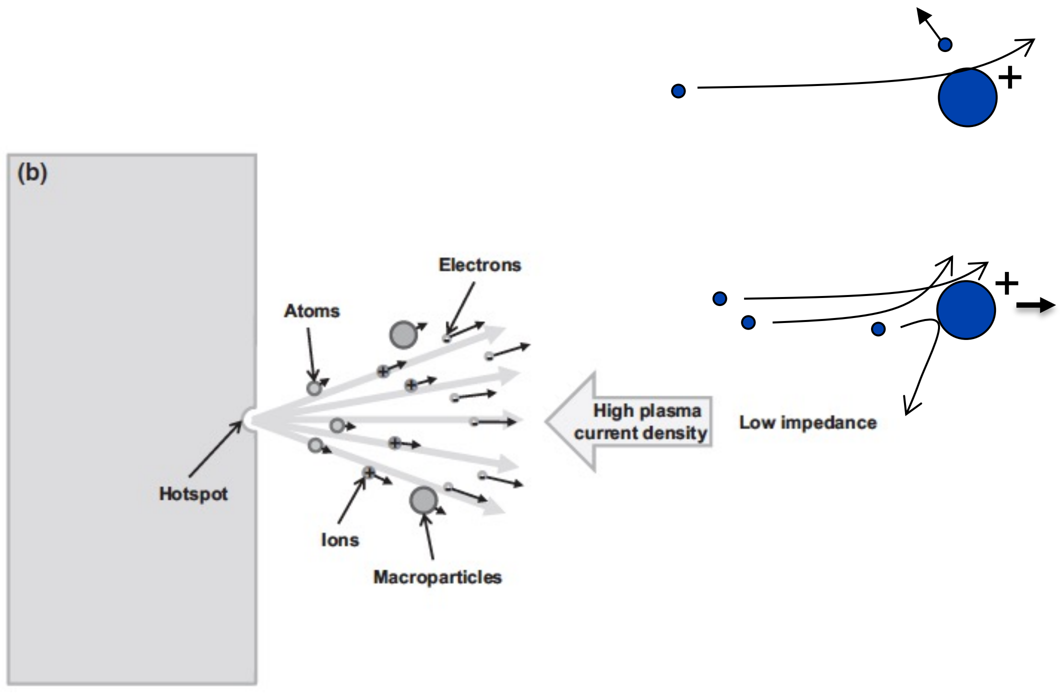


Figure 13 The evolution of the cathode spot in four stages. (a) Pre-explosion; (b) explosive stage; (c) cooling with molten cathode material; and (d) final cooling.

Koskinen, J. Cathodic-Arc and Thermal-Evaporation Deposition. In Comprehensive Materials Processing;Cameron, D., Ed.; Vol. 4; Elsevier Ltd., 2014, 2014; pp 3–55. ISBN: 9780080965321

Electron wind causes ionization and acceleration of atoms

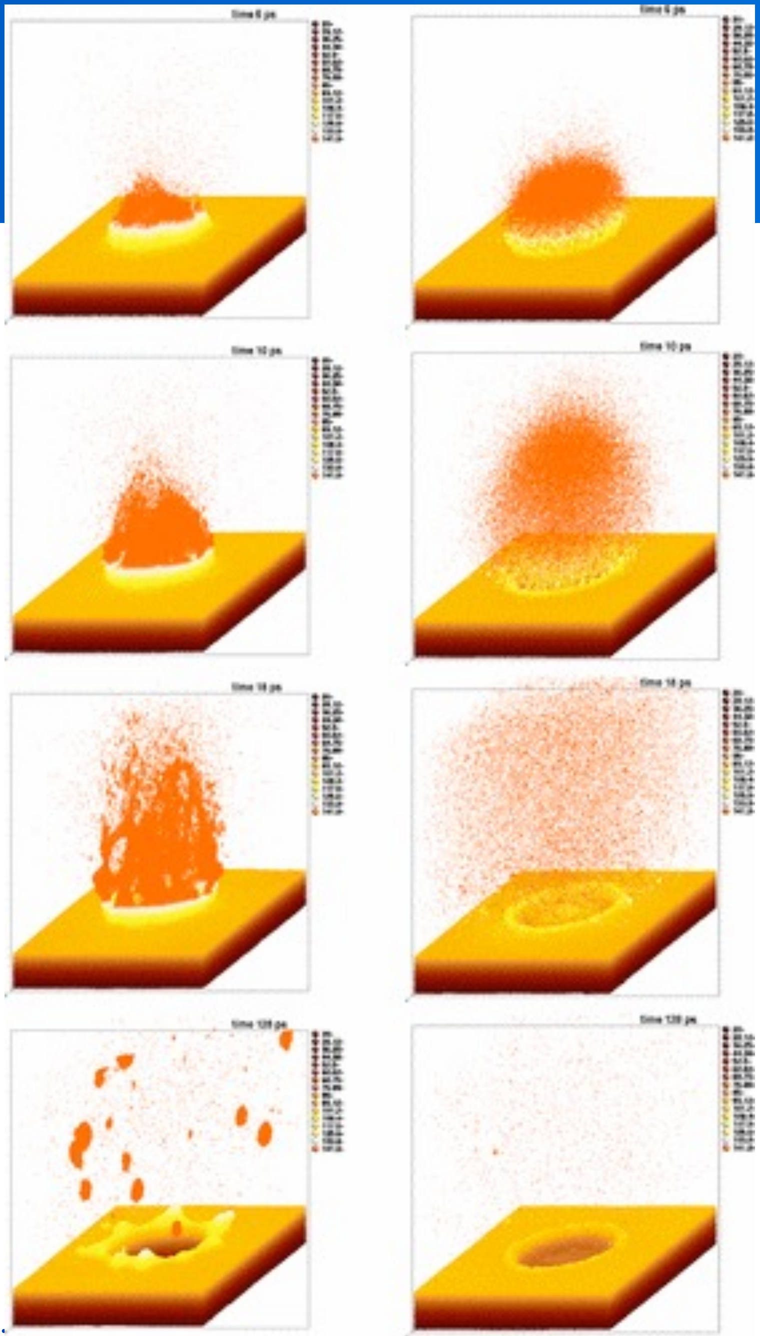


Ionization of atoms

Acceleration of ions

Koskinen, J. Cathodic-Arc and Thermal-Evaporation Deposition. In Comprehensive Materials Processing;Cameron, D., Ed.; Vol. 4; Elsevier Ltd., 2014, 2014; pp 3–55. ISBN: 9780080965321

Arc spot evolution by numeric simulation

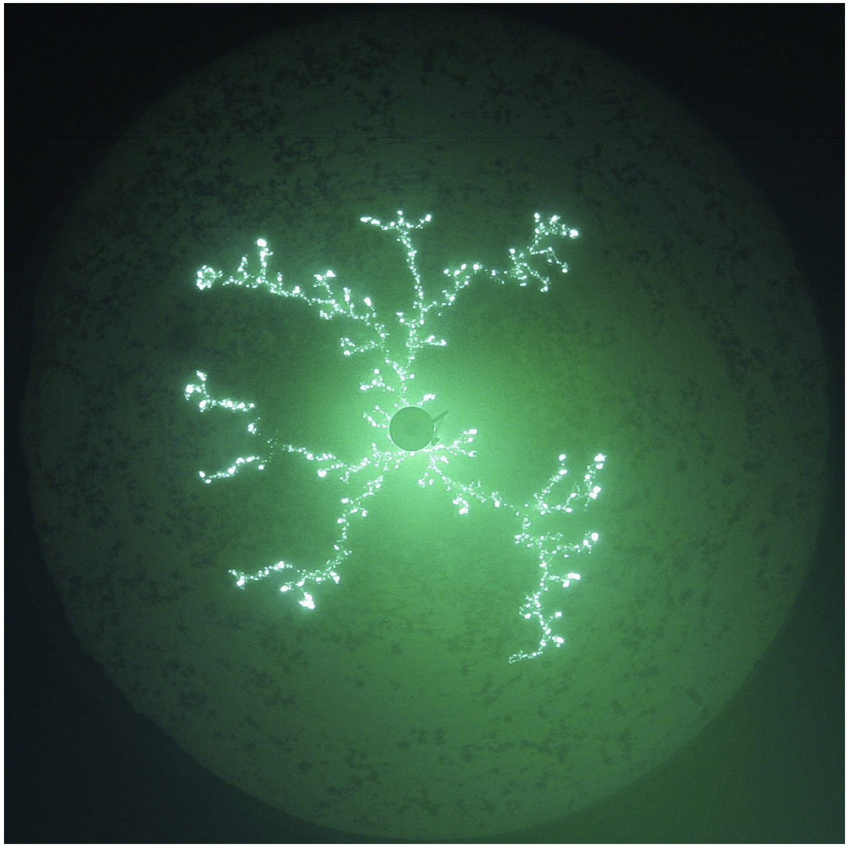


Left: energetic plasma ion flux

Right: local thermal heating

Koskinen, J. Cathodic-Arc and Thermal-Evaporation Deposition. In Comprehensive Materials Processing;Cameron, D., Ed.; Vol. 4; Elsevier Ltd., 2014, 2014; pp 3–55. ISBN: 9780080965321

Arc cathodic spot evolution

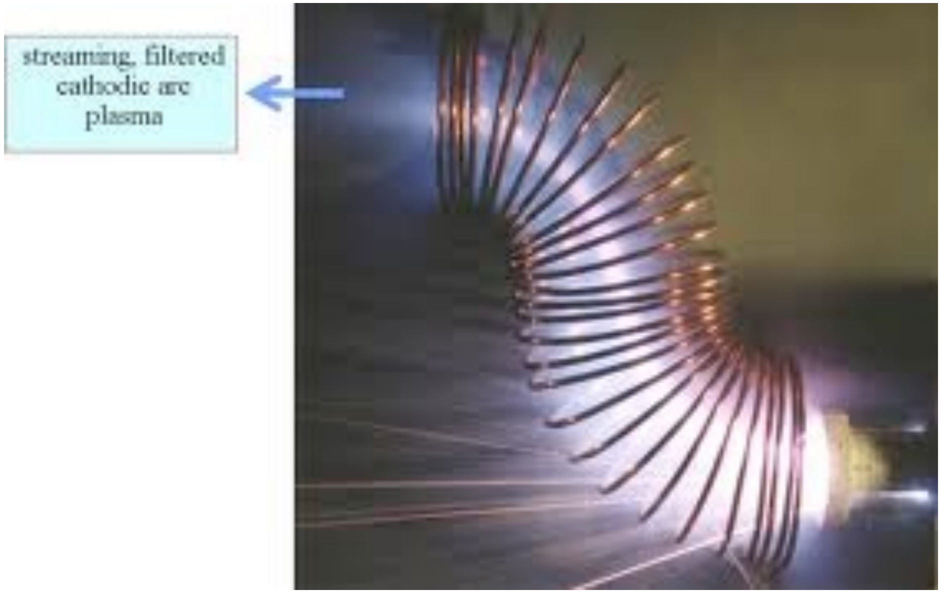


Arc spot traces of a pulsed arc on a Cu cathode. Photo courtesy and with permission of Dr Peter Siemroth.

Koskinen, J. Cathodic-Arc and Thermal-Evaporation Deposition. In Comprehensive Materials Processing;Cameron, D., Ed.; Vol. 4; Elsevier Ltd., 2014, 2014; pp 3–55. ISBN: 9780080965321

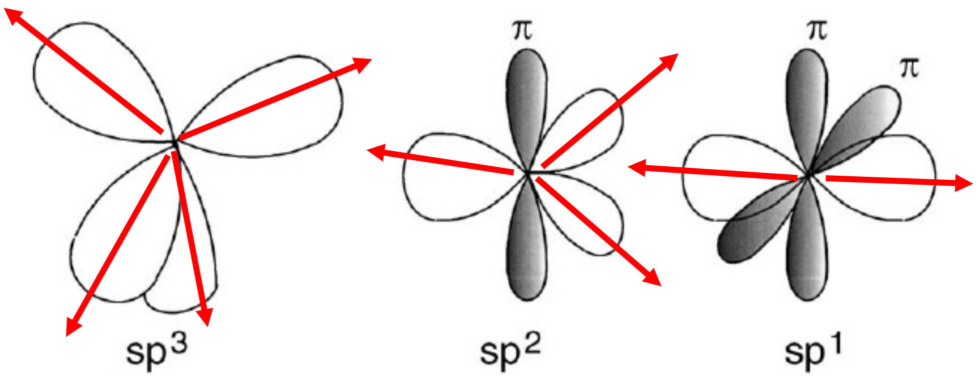
Filtering of particles from vacuum arc plasma

- plasma follows magnetic field lines
- plasma bent around corner
- particles go straight



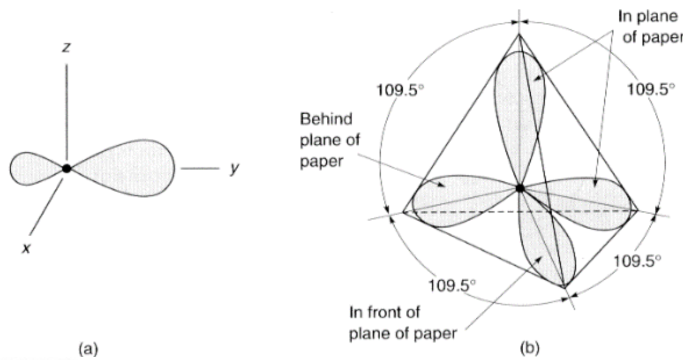
Andre Anders LBL

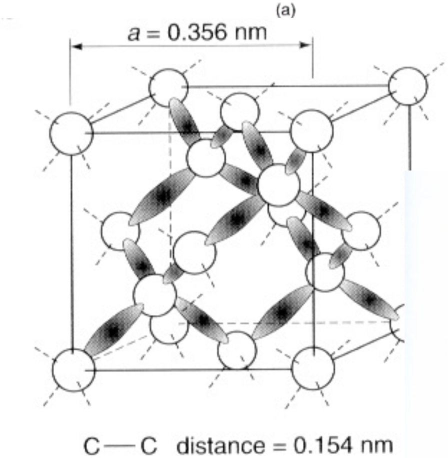
Three types of bonding of carbon atoms

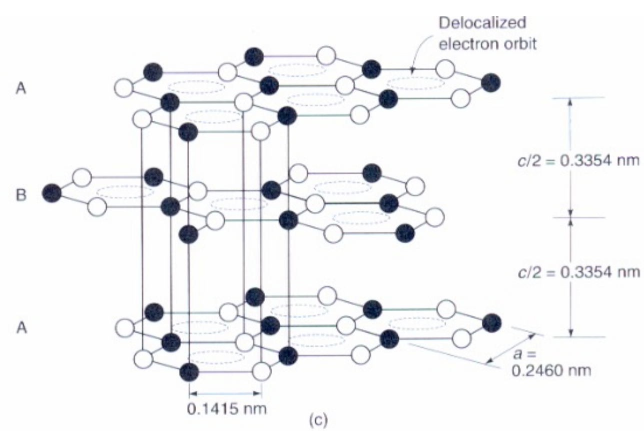


- **sp³**
  - Four string σ bonds in tetraedric directions
- **sp²**
  - Two σ bonds in plane
  - One weekπ bond (non localised electron- conductivity)
- **sp¹**
  - Two σ linear bonds
  - Two week π bonds (non localised electrons- conductivity)

Carbon



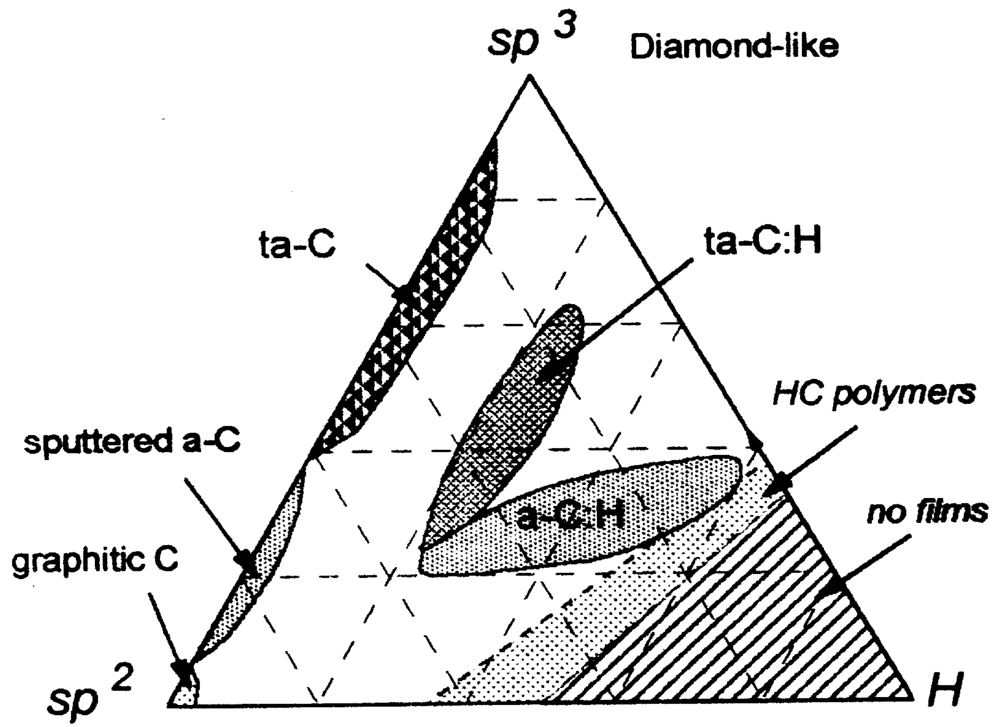




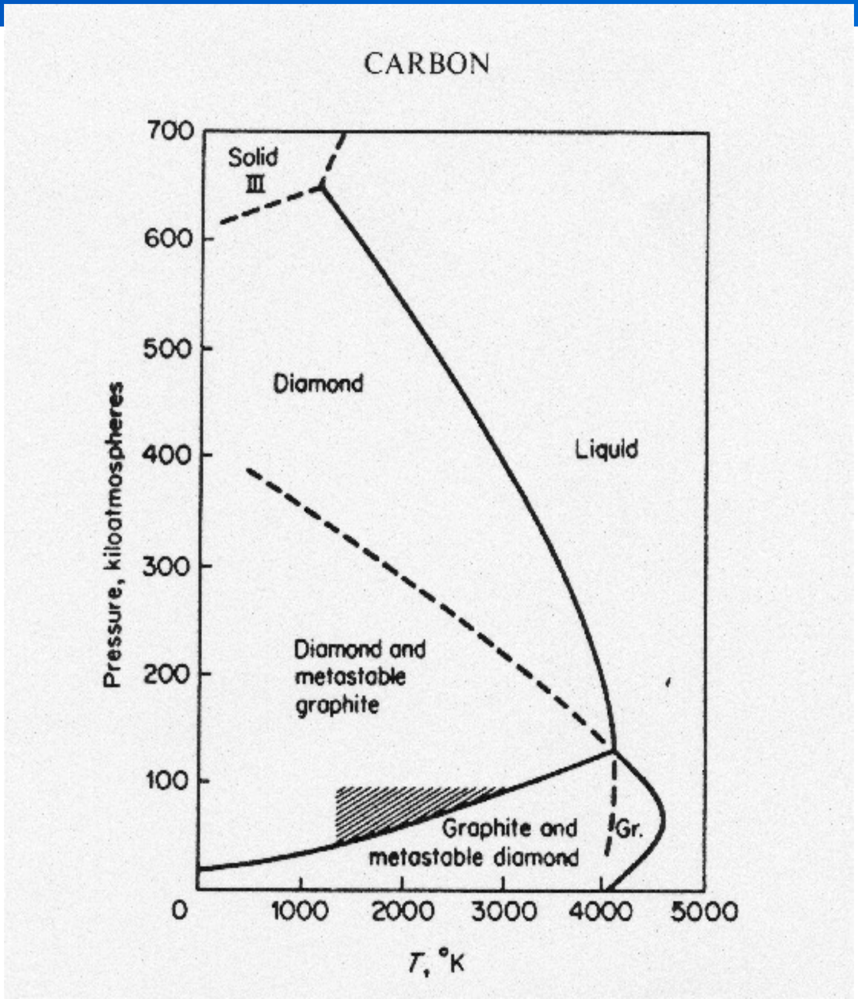
- **Carbon has 3 hybridised bondings sp^3, sp^2, sp^1**
- **sp^3 bondings form four equal carbon-carbon bonds producing tetrahedral structure of diamond**

Graphite has three sp^2 hybrid orbitals in plane

Diamond-like carbon (DLC)

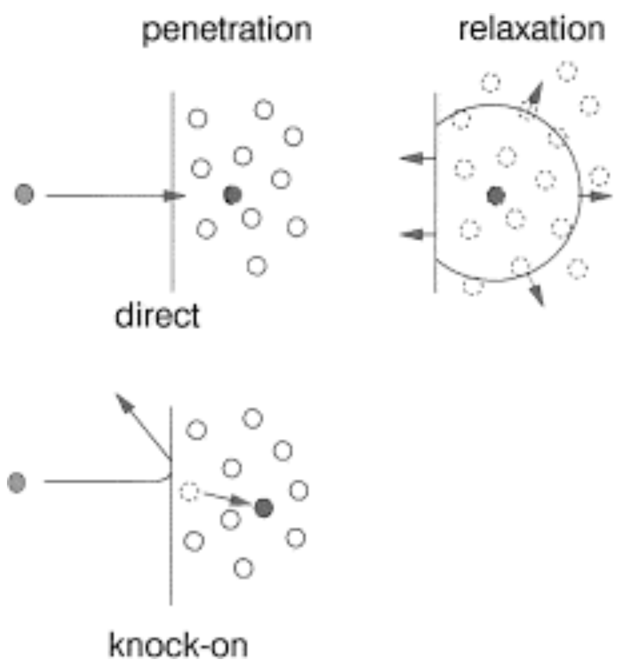


- Various forms of C-H alloys presented in a ternary phase diagram
- DLC is a metastable form of amorphous carbon
- DLC films have a mixed sp^3/ sp^2 structure with different sp^3 and sp^2 proportions depending on deposition technique and parameters



CARBON
700
600
500
400
300
200
100
0
1000
2000
3000
4000
5000
Pressure, kiloatmospheres
T, °K
Solid III
Diamond
Liquid
Diamond and metastable graphite
Graphite and metastable diamond
Gr.

Subplantation



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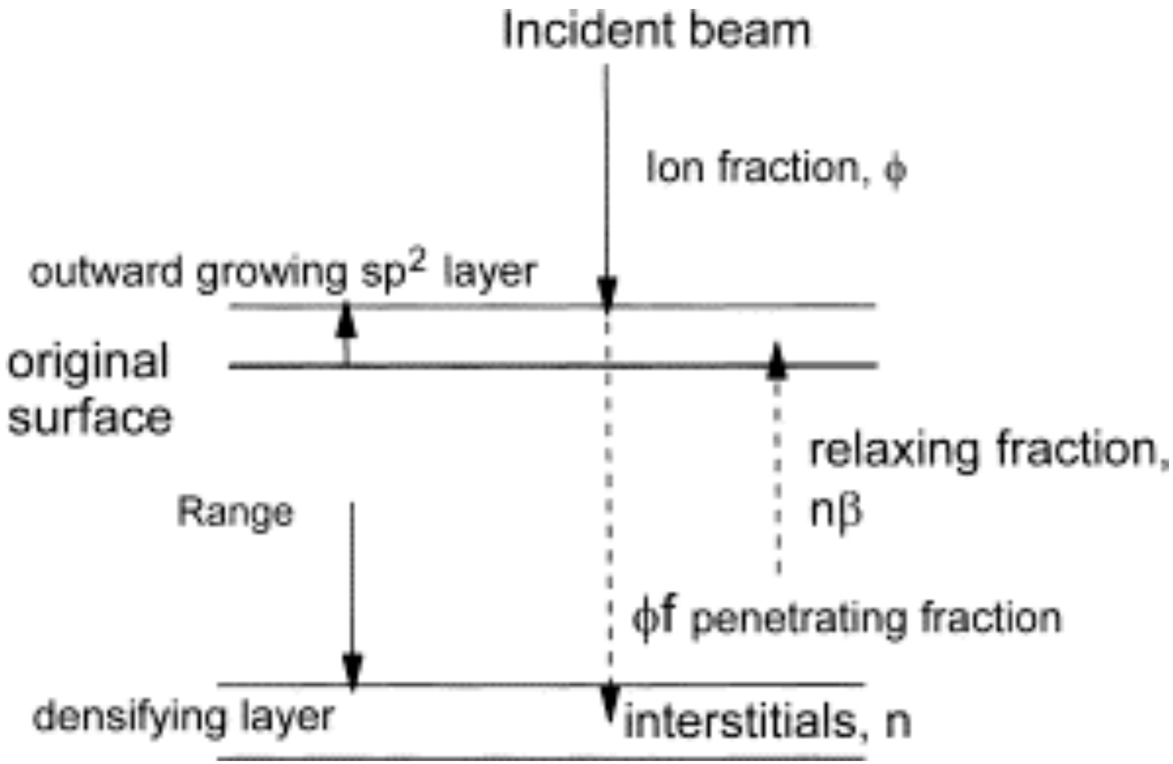
Subplantation



Schematic diagram of densification by subplantation. A fraction of the incident ions penetrate the film and densify it, the remainder end up on the surface to give thickness growth.

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Subplantation -> Ion peening

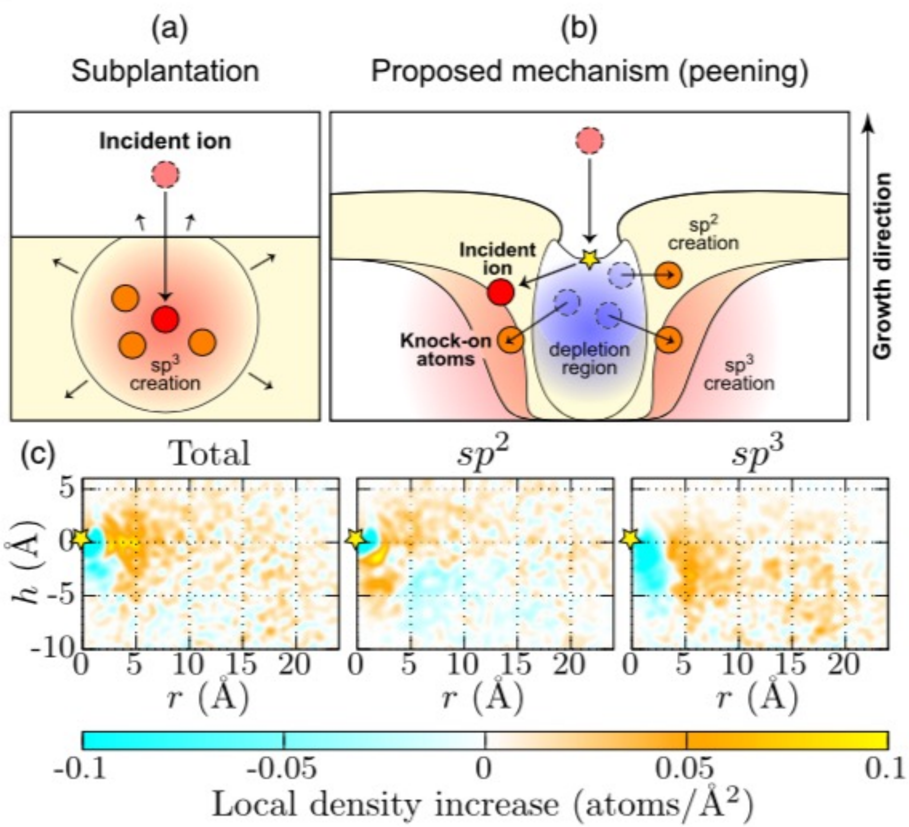
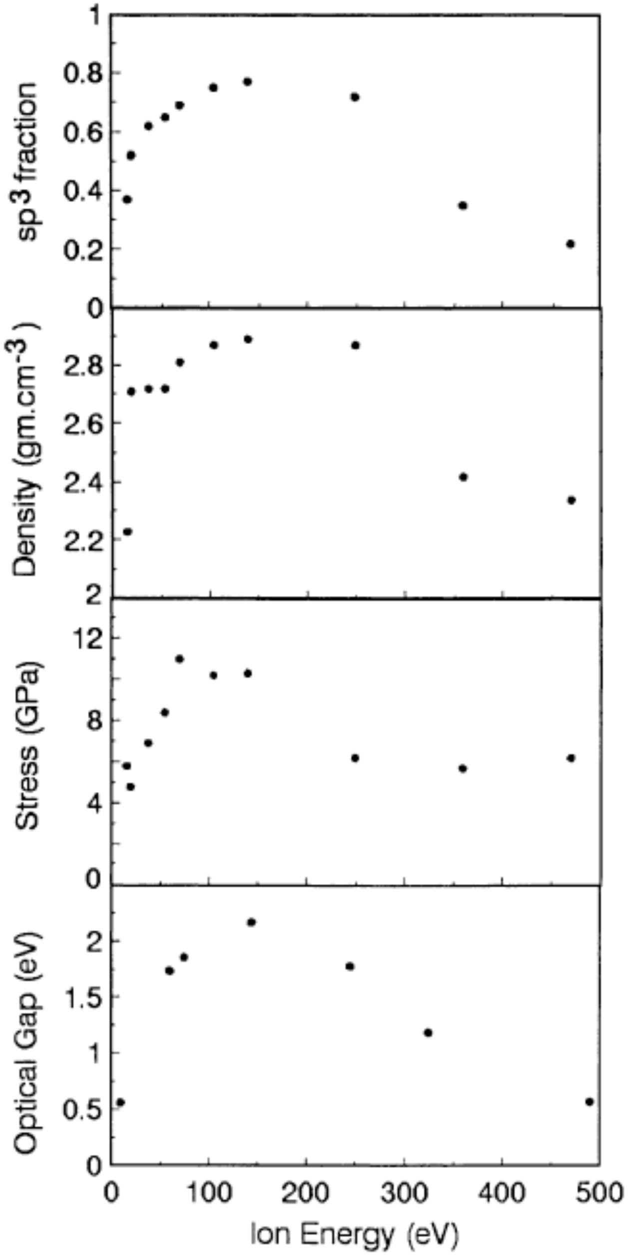


FIG. 4. (a) Previously accepted growth mechanism in ta-C and (b) growth mechanism proposed in this Letter. (c) Average increase in local mass density after ion impact (60 eV deposition; see text for details). The star indicates the impact site.

Miguel A. Caro, Volker L. Deringer,
Jari Koskinen, Tomi Laurila, Gábor Csányi,
PHYSICAL REVIEW LETTERS 120, 166101 (2018)

Properties of ta-C as function of E_i



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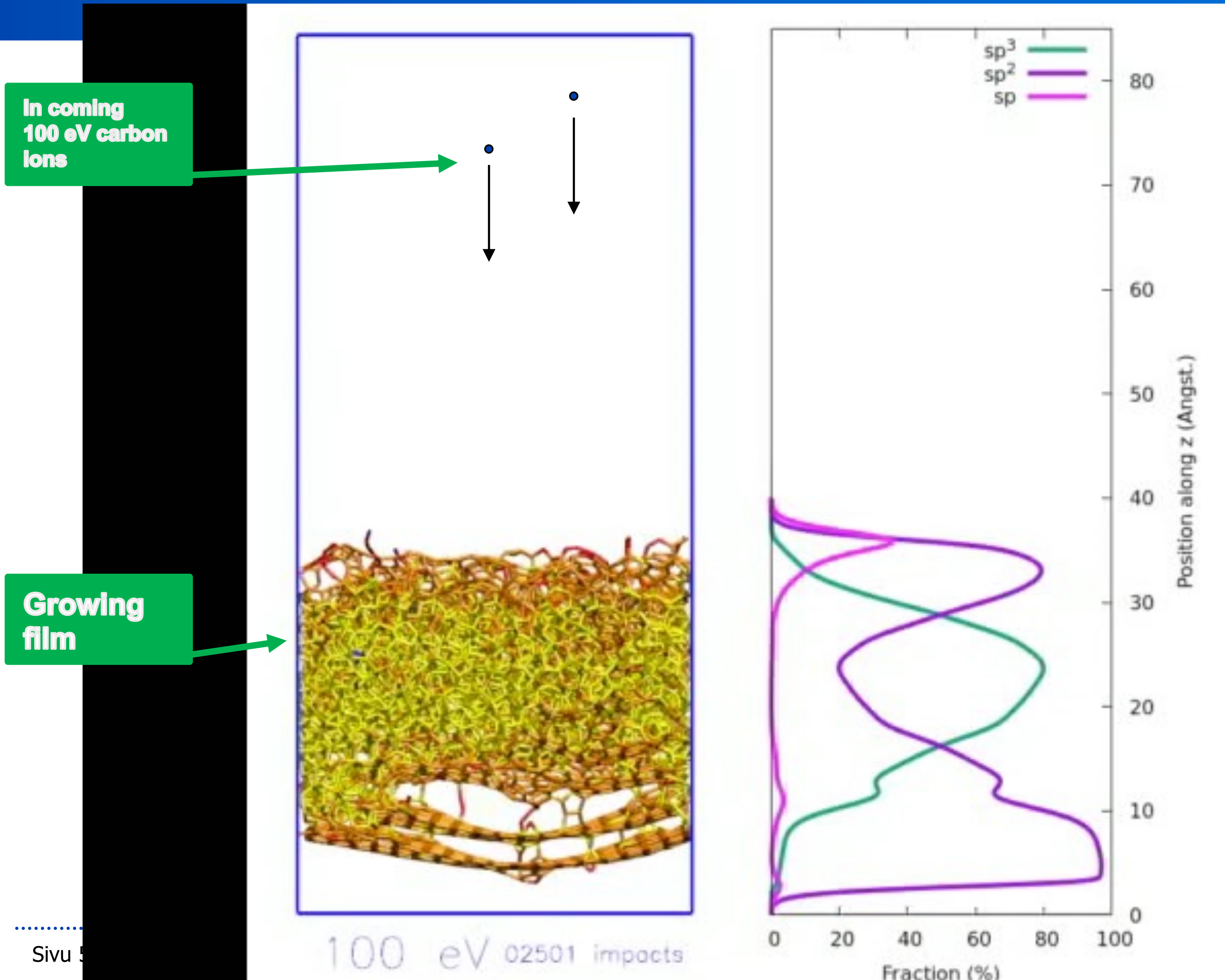
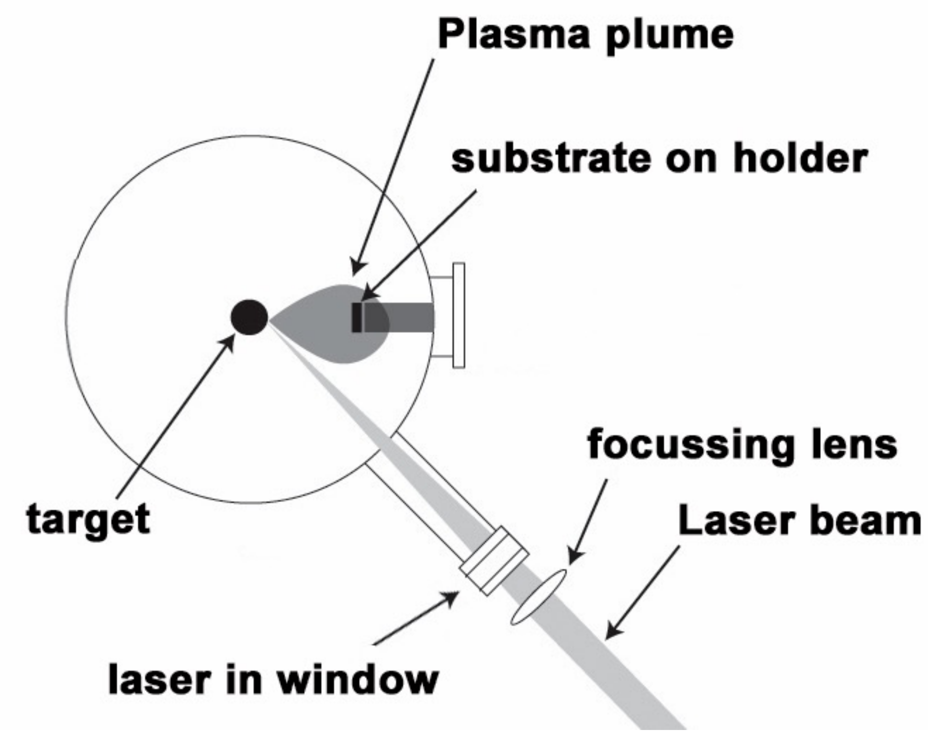
Ta-C film growth molecular dynamic simulation, Miguel Caro https://zenodo.org/record/1133425

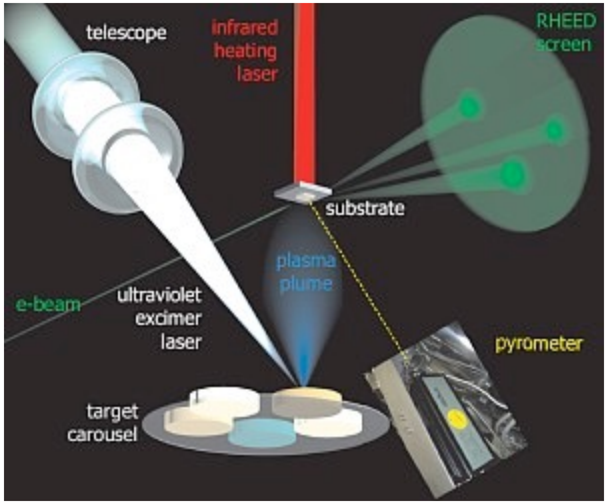


Pulsed laser deposition PLD

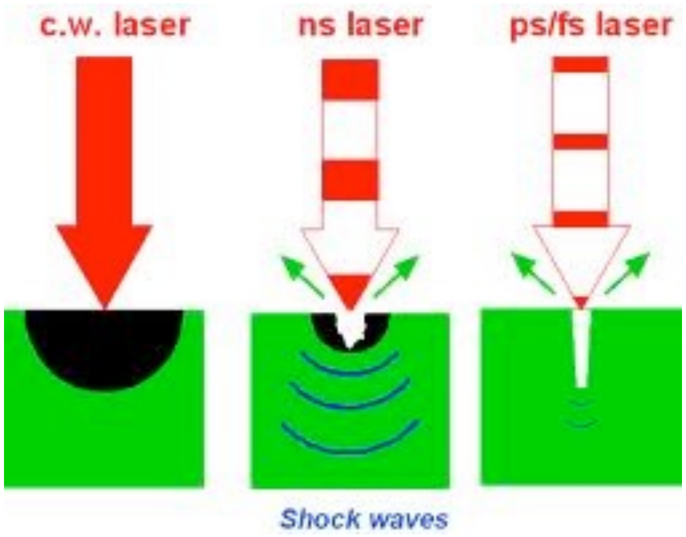


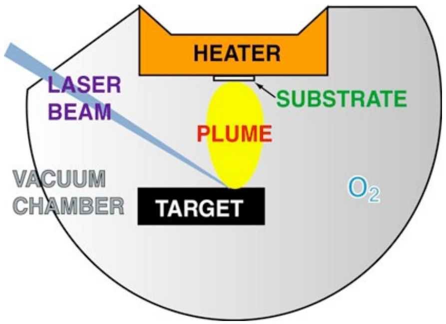
http://www.youtube.com/watch_popup?v=g9RM4QhBnL0&vq=medium#t=19

- high ionization
- evaporation of any material also in reactive gas
- stoichimetry of target to the surbstrate
- good control of depostion rate
- expensive lasers
- slow depostion rate
- not yet in industrial level

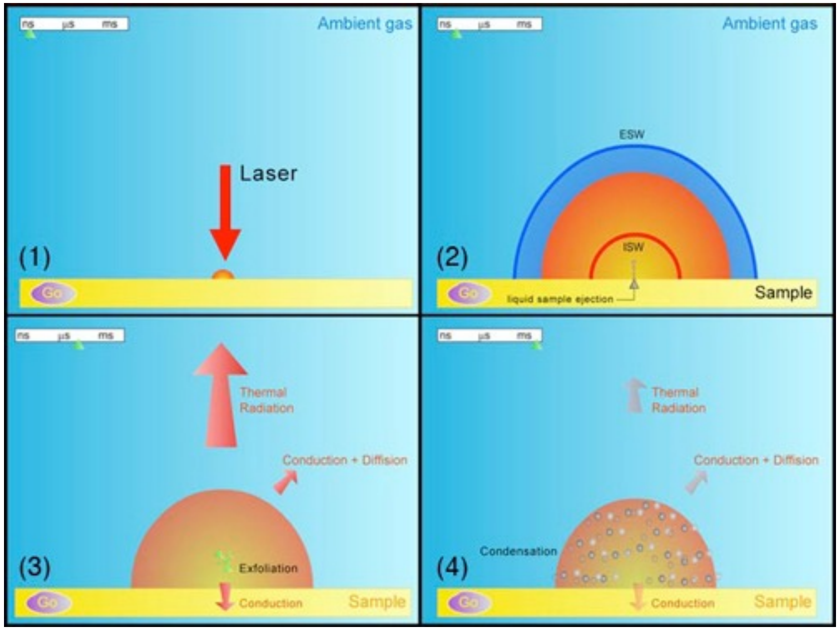


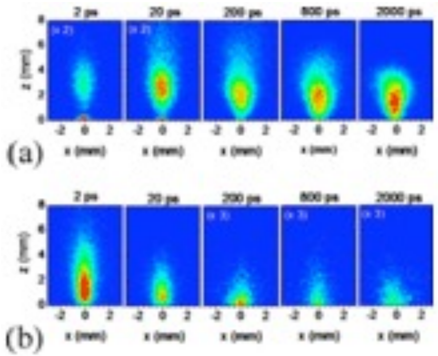
Laser ablation





Plasma plume





- Copper target

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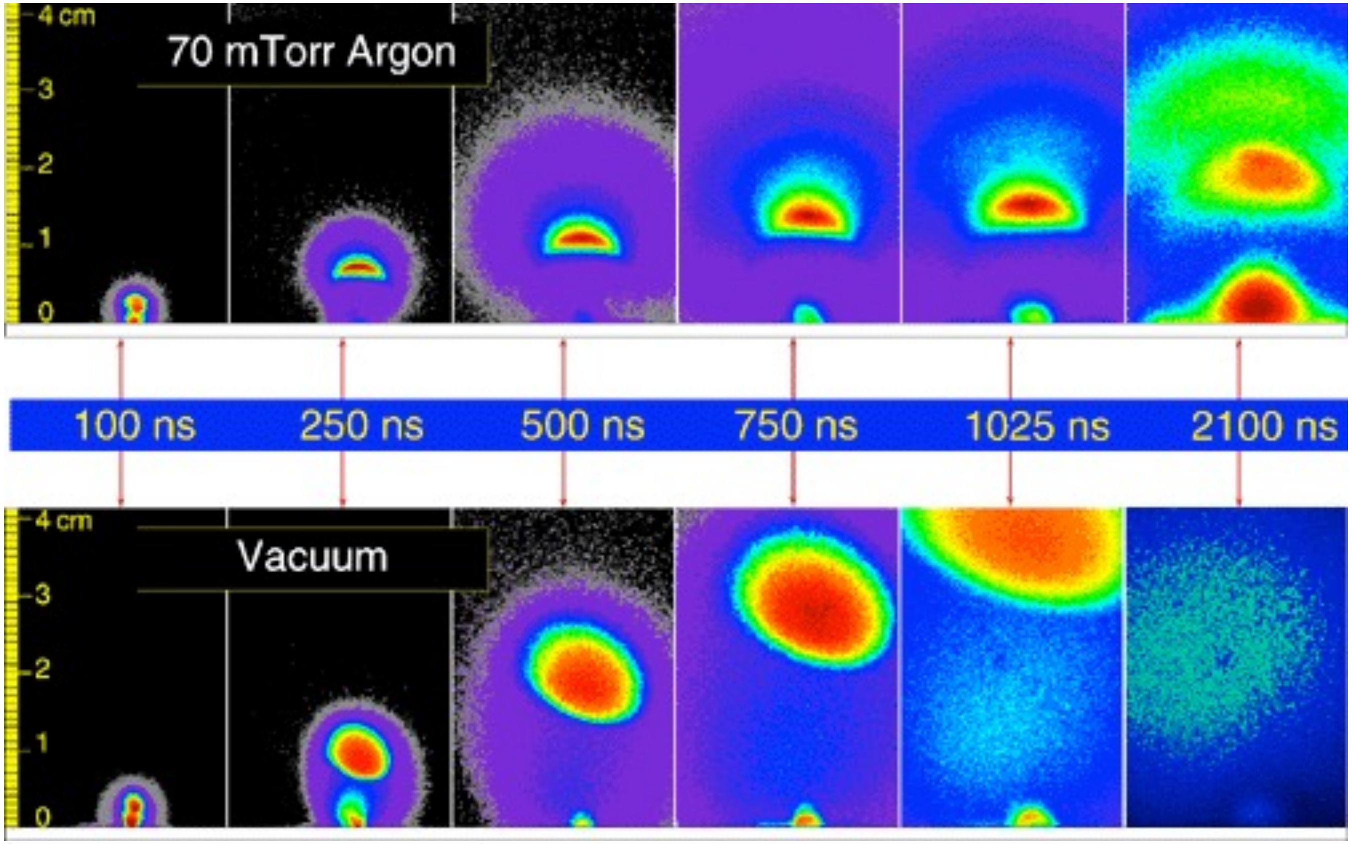
Laser plasma plume



- Carbon plasma from graphite target

Particularly suitable for alloyed materials

Thin films made by the PPD
• Transparent Conducting Oxides (TCO) (ITO, IMO, ZnO, etc.)
• Multi layer thin film solar cells (CdS, CdTe, Sb_2Te_3, $CuInSe_2$, etc.)
• High TC superconductors (YBCO ,T_C > 92K, $I_C = 2\text{-}4 \cdot 10^6$ A/cm^2)
• CMR manganites (T_C = 350 K, 100% spin polarized at room temperature)
• Ultra high k dielectrics (BST, STO, etc.)
• Buffer layers (AlO_x, TiO_x, CeO_x, $SrTiO_3$, BaF_2, etc.)
• High bandgap materials (SiO_x,etc)
• Biocompatible materials (quaternary SiO_2- CaO- P_2O_5- Na_2O system)
• Organic materials (teflon, polyethylene, etc.)
• Hard and wear resistant coatings (SiC, TiN, Diamont like Carbon, etc.)

Organic Spintronics

E_i as a function of laser pulse energy

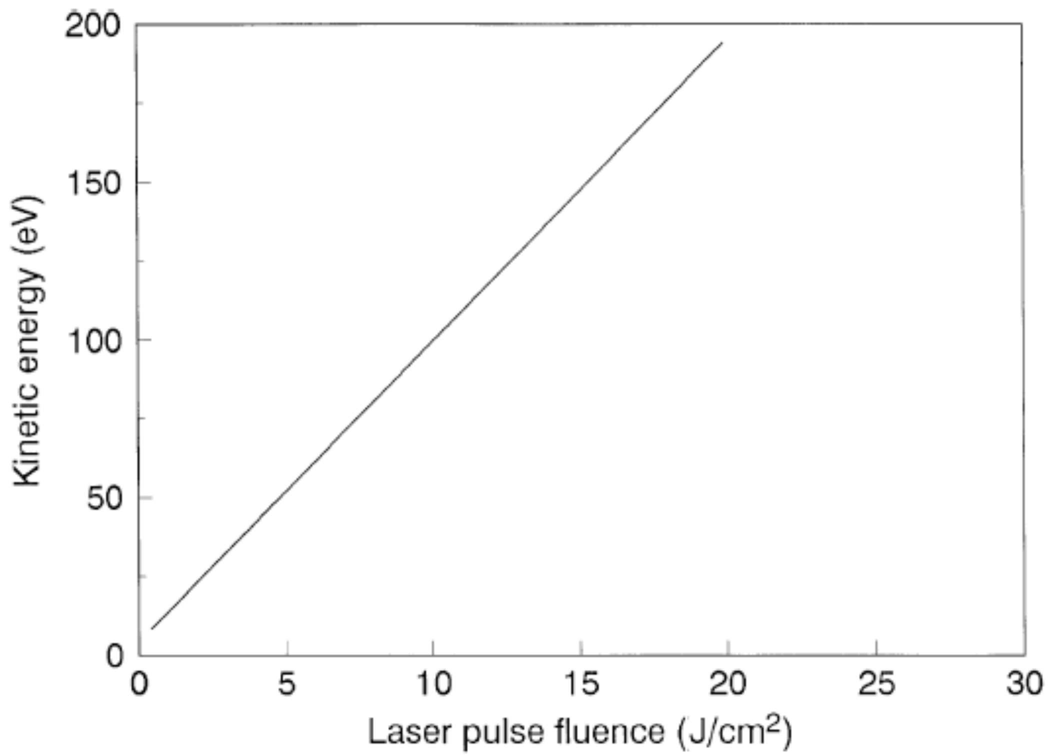


Fig. 6. Average ion energy vs. laser pulse fluence [9].

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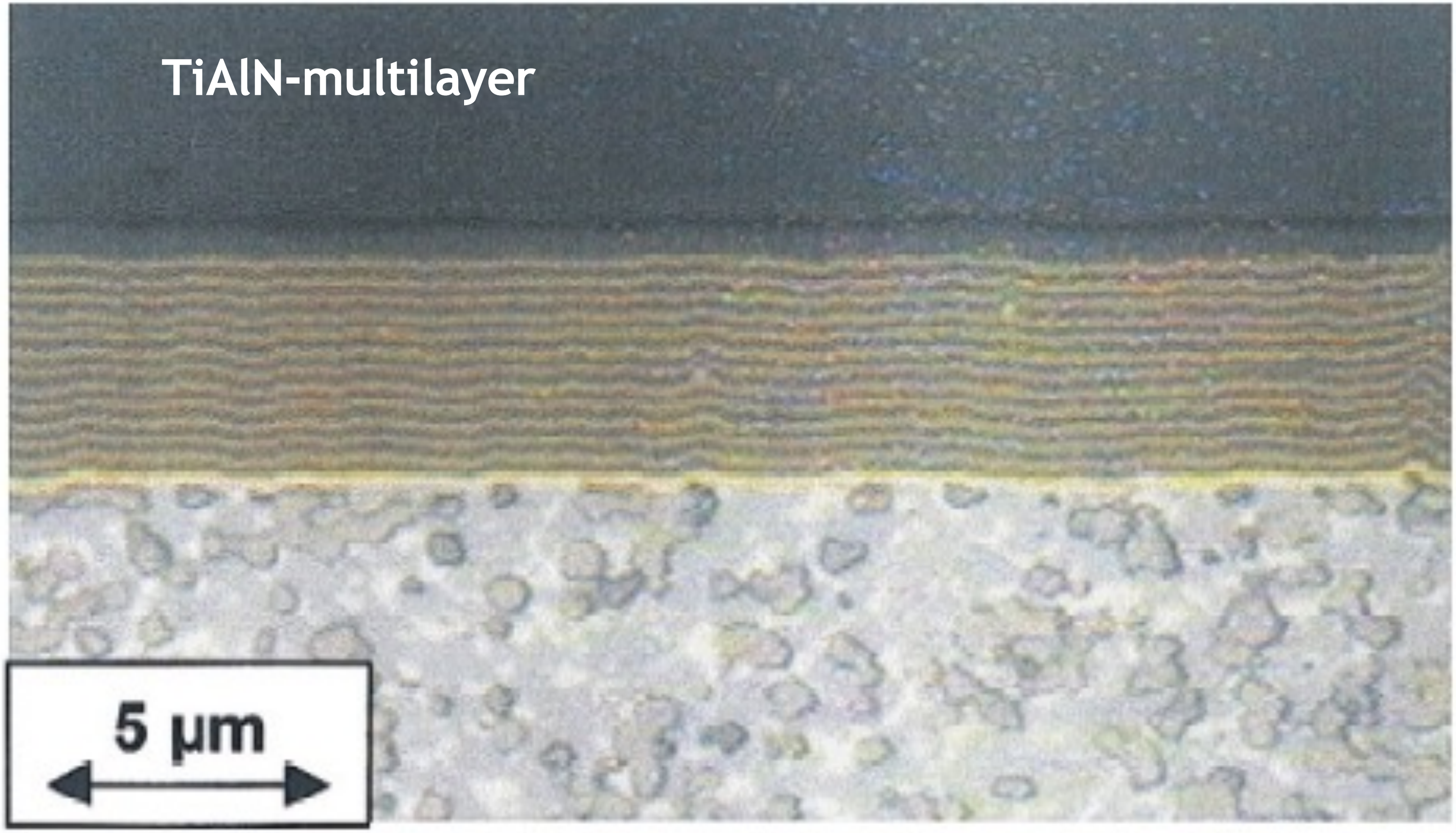
Multilayer coatings



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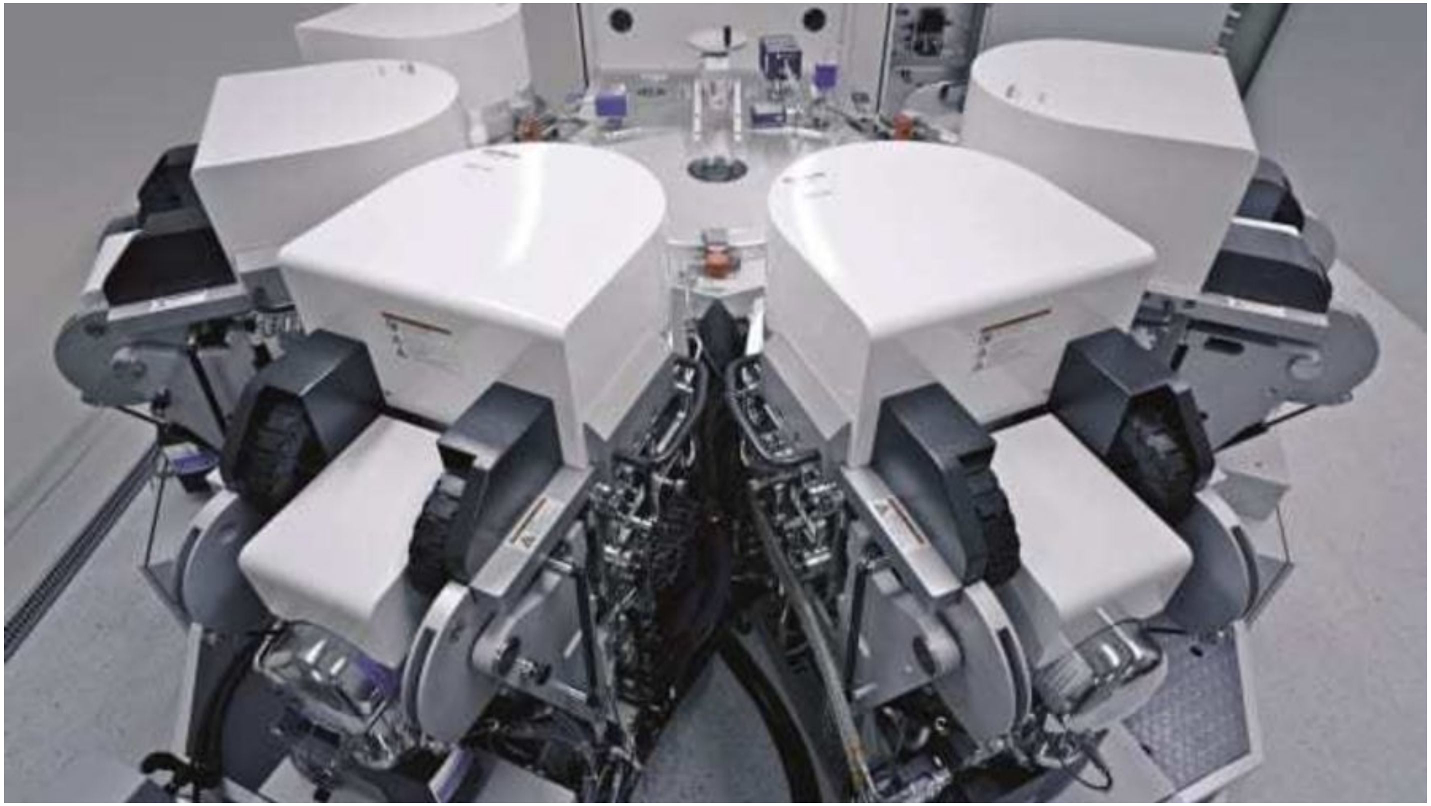
Contents

- Plasma
- Ion surface interactions
- Film growth mechanisms
- Different PVD methods
- Commercial PVD coatings
- **Scale up**

Commercial PVD

- Oerlikon Balzers. **CLUSTERLINE® 300** **thin films for 300 mm wafers**



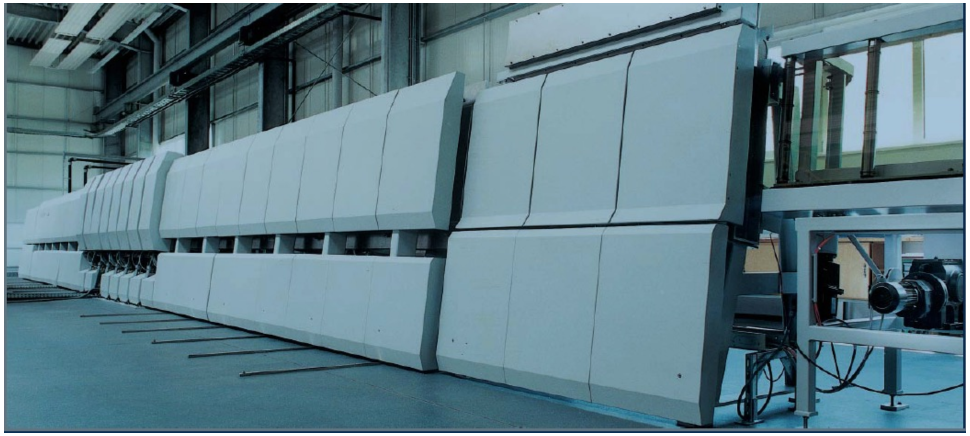
Hauzer

Hauzer Triboliner inline coating system

https://www.hauzertechnocoating.com/en/products/inline-coating-systems/triboliner/

- Horizontal inline system
- Cathodes are mounted above the transport line
- Magnetron sputtering
- Dual magnetron sputtering
- HiPIMS.

Large volumes, up scaling
Heat reflecting, self cleaning, photo voltaic



/www. www.vonardenne.biz/

New emerging PVD methods

- vacuum polymer deposition (VPD)
- high-power pulsed magnetron sputtering (HPPMS or HIPIMS)
- filtered cathodic arc deposition
- glancing angle deposition (GLAD).